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Analytical Determination of Fluorides in South African Chemical Gypsum.

By

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God is great

Abstract

Fluoride ion is an accompanying impurity in a wide variety of chemical gypsum throughout the world. In this study, the Ion Selective Electrode (ISE) method, the Ion Chromatography (IC) method and the standard Willard and Winter method of fluoride analysis were adapted and compared for use in the quantification of fluoride in South African chemical gypsum.

During the use of ISE, the pH of sample solutions was found to be a critical parameter for the results to be meaningful. An operating pH of approximately 5 was suitable for consistency of results. It was important to ensure the existence of the ionised form of fluorine in solution, because the detection was based on the sensitivity of the membrane electrode to this species. In the case of the Willard and Winter method, the traditional visual indicator titration was replaced by a more sensitive spectrophotometric detection, because of low fluoride levels in the chemical gypsum. The parameter sensitive reaction rate approach was adapted, and the reaction allowed to go to completion to enable measurement with a bench top spectrophotometer. The IC method required a good separator since fluoride ions usually eluted too early for detection on common ion exchange columns. The data handling of the chromatographic software was thoroughly examined and consistent integration of the chromatograms maintained.

Sample preparation of the chemical gypsum involved particle size reduction through grinding. No trend between fluoride impurity and the particle size of the sample was observed.

The quantity of fluoride in Kynoch and Omnia phosphogypsum were found to be 0.10% and 0.04% respectively. The Tioxide chemical gypsum, titangypsum, was found to contain in the region of 0.02% fluoride. Generally, the level of fluorine (F) has to be reduced to about 0.2% before phosphogypsum can be used as substitute for natural gypsum in the cement industry.

The aim of this study is to critically evaluate three analytical methods, namely, the Willard and Winter standard method of fluoride analysis, the ISE method, and IC as applied in the quantification of fluoride in chemical gypsum. Secondly, the efficiency of treatment of the chemical gypsum with water, lime and sulphuric acid was investigated.

The ISE method was found to be faster and relatively simpler versus both Willard and Winter and the IC methods. The IC method was quite superior for indicating general complexity of the sample and it was faster than the Willard and Winter method. The standard Willard and Winter method was generally found to be long and tedious. The three methods validated one another as percentages of fluoride in the chemical gypsum samples were the same.

The study indicated that a sulphuric acid pretreatment of the chemical gypsum was the most effective (90%) in the removal of fluoride impurity compared to the lime treatment and water washing (9%). However, the water washing would be inexpensive for practical treatment of chemical gypsum at plant level.

Samevatting

Flouriedioon word aangetref as 'n begeleidende onsuiwerheid in 'n wye verskeidenheid chemiese gipse. In hierdie studie word die Ioonselektiewe elektrode (ISE) metode, die Ioonchromatografie (IC) metode en die standaard Willard en Winter metode, vir die analise van fluoried, aangepas en vergelyk vir toepassing in die kwantifisering van fluoried in Suid-Afrikaanse chemiese gips.

Deur gebruik te maak van die ISE metode, is gevind dat die pH van die monsteroplossings 'n kritiese parameter is sodat betekenisvolle resultate verkry kon word. 'n pH van ongeveer 5 was geskik om konsekwente resultate te verkry. Dit was belangrik om die geïoniseerde vorm van fluoried in die oplossing te verseker, aangesien die bepaling gebaseer was op die sensitiwiteit van die membraan elektrode vir hierdie spesie. As gevolg van die lae fluoried vlakke in chemiese gips, is die tradisionele visuele indikator titrasie in die geval van die Willard en Winter metode vervang deur 'n meer sensitiewe spektrofotometriese bepaling. Die parameter sensitiewe reaksietempo benadering is aangepas, en die reaksie is toegelaat om volledig plaas te vind ten einde die bepaling met behulp van 'n bankspektrofotometer uit te voer. Die IC metode het 'n goeie skeier vereis aangesien die fluoriedione gewoonlik te vroeg elueer vir waarneming op algemene ioonuitruilkolomme. Die data hantering van die chromatografiese sagteware was deeglik ondersoek en konsekwente integrasie van die chromatogramme was gehandhaaf.

Die hoeveelheid fluoried in die Kynoch en Omnia fosfogips was 0.10% en 0.04% respektiewelik. Die Tioksied chemiese gips, titaangips, het ongeveer 0.02%

fluoried bevat. Gewoonlik moet die vlak van fluoor (F) na ongeveer 0.2% verminder word, voordat fosfogips as plaasvervanger vir natuurlike gips in die sement industrie gebruik kan word.

Die doel van hierdie studie is om drie analitiese metodes, naamlik die Willard en Winter standaardmetode vir fluoried analise, die ISE metode, en IC, krities te evalueer soos toegepas in die kwantifisering van fluoried in chemiese gips. Tweedens is die effektiwiteit van die behandeling van chemiese gips met water, kalk en swaelsuur ondersoek.

Daar is vasgestel dat die ISE metode vinniger en relatief eenvoudiger is as beide die Willard en Winter en die IC metodes. Die IC metode kon die algemene kompleksiteit van die monster beter aantoon, en was vinniger as die Willard en Winter metode. Die standaard Willard en Winter metode was in die algemeen lank en tydsaam. Aangesien die persentasie fluoried in al die chemiese gips monsters dieselfde was, kon die drie metodes mekaar valideer.

Die studie het aangetoon dat voorafbehandeling van die chemiese gips met swaelsuur die effektiefste (90%) was in die verwydering van fluoried onsuiwerhede, in vergelyking met beide water (9%) wassing en behandeling met kalk. Wassing met water is egter goedkoper vir die praktiese behandeling van chemiese gips op aanleg vlak.

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Table of abbreviations used in the text

Abbreviation	Full name
ISE	Ion Selective Electrode
IC	Ion Chromatography
TWQR	Target Water Quality Range
HPLC	High performance liquid chromatography
HPIC	High performance ion chromatography
HPICE	High performance ion chromatography exclusion
MPIC	Mobile phase ion chromatography
AAS	Atomic absorption spectrometry
TCG	Tioxide chemical gypsum
TCGU	Tioxide chemical gypsum unwashed
TCGW	Tioxide chemical gypsum water washed
TCGL	Tioxide chemical gypsum lime washed
PRSU	Phosphate rock sample unwashed
FPSU	Filter pan sample unwashed
FPSW	Filter pan sample water washed
FPSL	Filter pan sample lime washed
KYN2SUL-GH4	H_2SO_4 treated Kynoch phosphogypsym
OM2SUL-GH4	H_2SO_4 treated Omnia phosphogypsym
TISAB	Total ionic strength adjustment buffer
PH	Peak height
PA	Peak Area
RSD	Relative standard deviation
DSC	Differential scanning calorimetry

Chapter 1 Chemical Gypsum: Background

1.1 Definitions

Chemical gypsum is broadly defined as the by-product gypsum or co-product gypsum produced from a variety of industries. The following are examples of chemical gypsums:

- phosphogypsum is a by-product of the phosphate fertilizer industry. It is produced from the sulphuric acid attack on the phosphate rock in the initial stage of phosphoric acid production (Bensted, 1979; Mehta and Brady, 1977; Roode, 1996; Rutherford et. al., 1995). This type of chemical gypsum will be discussed in Section 1.2.
- fluorogypsum is a by-product of the manufacture of hydrofluoric acid (Murakami, 1968). It is produced by the reaction of fluorspar (fluorite) and sulphuric acid. The chemical reactions are:

  $$CaF_2(s) + H_2SO_4(aq) \rightarrow 2HF(aq) + CaSO_4(\text{anhydrite})(s)$$

  $$CaSO_4(s) + 2H_2O(l) \rightarrow CaSO_4{\cdot}2H_2O(s).$$

- titangypsum is a co-product in the manufacture of titanium dioxide pigment (Murakami, 1968). It is produced from the limestone treatment of the waste stream. The relevant chemical reactions are given in Section 1.6.

- chemical gypsum is also produced in the neutralization of $CaCO_3$ and $Ca(OH)_2$ with waste sulphuric acid during the pickling process in the manufacture of iron (Murakami, 1968).

$CaCO_3(s) + H_2SO_4(aq) + H_2O(l) \rightarrow CaSO_4{\cdot}2H_2O(s) + CO_2(s)$

$FeSO_4(aq) + Ca(OH)_2(s) + 2H_2O(l) \rightarrow CaSO_4{\cdot}2H_2O\ (s) + Fe(OH)_2(s)$

- chemical gypsum is also produced via the oxidation and neutralization reactions of SO_2 in combustion and exhaust gases emitted by various industries and power plants (Murakami, 1968).

  $2SO_2(g) + 2Ca(OH)_2(s) \rightarrow 2CaSO_3{\cdot}1/2H_2O(s) + H_2O(l)$

  $2CaSO_3{\cdot}1/2H_2O(s) + O_2(g) + 3H_2O(l) \rightarrow 2CaSO_4{\cdot}2H_2O(s)$

In this study, phosphogypsum and titangypsum are the materials of primary focus. Samples of these gypsums were obtained from South African companies which produce them as waste.

1.2 Phosphogypsum

Phosphogypsum is the acidic by-product derived from the phosphate fertilizer industry. In this industry, phosphoric acid is synthesized and then used in the production of a variety of phosphate fertilizers. Phosphoric acid is produced either by the electric furnace method, which uses electrical energy to produce elemental P as a first stage, or by the wet process which uses sulphuric acid attack (Rutherford et. al., 1995). The latter method is used widely throughout the world for phosphoric acid production (Mathias and Mendez, 1998; Rutherford et. al., 1995).

1.2.1 Production Process

The phosphoric acid production process initially involves the mining of the phosphate rock which includes calcium, phosphates, and a number of impurities. The phosphate rock is then treated with a physical process called beneficiation. This involves concentration by washing, screening and flotation (Mathias and Mendez, 1998; Rutherford et. al., 1994). Calcination, the crushing and heating of the rock to temperatures as high as 950 °C, may be required to reduce the organic content. The rock is sometimes ground dry or wet by means of ball mills or rod mills. The rock is then fed into an attack tank or reactor and digested with sulphuric acid.

The reaction for the wet method (dihydrate process) for phosphoric acid production can be simplified as (Rutherford et. al., 1994;Rutherford et. al., 1995):

$$Ca_{10}(PO_4)_6F_2(s) + 10H_2SO_4(aq) + 20H_2O(l) \rightarrow 10CaSO_4{\cdot}2H_2O(s) + 6H_3PO_4(aq) + 2HF(aq).$$

The above reaction indicates that phosphogypsum is mainly gypsum ($CaSO_4{\cdot}2H_2O$). The phosphoric acid thus produced is separated from the phosphogypsum residue by the process of filtration. This phosphogypsum residue is washed with water and then sluiced out, using process water, to repositories for storage. On land, the phosphogypsum may be disposed to a sedimentation pond or it may be dried and stacked (de Freitas and Albuquerque, 1991;Wirsching, 1982; Wissa and Fuleihan, 1993). In some cases the phosphogyspum residue is sluiced out with process water into the sea or rivers (de Freitas and Albuquerque, 1991; Wirsching, 1982). The phosphoric acid is concentrated for optimum fertilizer production and stored in large tanks (Morris, 1993). The hydrofluoric acid produced reacts with undissolved silicates to form silicon tetrafluoride (SiF_4), which hydrolyzes to form fluorosilicic acid (H_2SiF_6) (Rutherford et. al., 1994). The high temperatures used in the process may allow the fluoro acids to decompose to gaseous HF and SiF_4. These are recovered as fluorosilicic acid by absorption in the water using scrubbers. Cargill

Fertilizer in the United States of America is the largest producer of fluoride for water treatment in the United States (Morris, 1993).

During the wet process of phosphoric acid manufacture, approximately 4 to 6 tonnes of phosphogypsum are produced for each ton of phosphoric acid (P_2O_5) (Freitas and Albuquerque, 1991). Generally, the plants operate on a 24 hour basis.

The degree of calcium sulphate hydration depends on the operating acid and temperature (Rutherford et. al., 1994) and may increase during transport and storage of the phosphogypsum. The hemi-hydrate process ($CaSO_4 \cdot 1/2H_2O$) produces a purer quality of acid concentration, between 32% and 52% (Rutherford et. al, 1994; Gadalla et. al, 1990). This process was initiated in Japan and subsequently adopted in Europe, but is used only to a limited extent in the United States. Adjusting the operating conditions to produce $CaSO_4$ in the form of hemihydrate produces purer material because phosphorous cannot be occluded in the crystal lattice. The hemihydrate process requires a low amount of energy and yields large crystals which can easily be filtered and washed. The hemihydrate changes to a dihydrate during transportation to stockpiles (Gadalla et. al., 1990). The material consists largely of clinkerlike agglomerated particles which become cemented in a fashion which does not allow easy access to parts of the pile other than the immediate surface, unlike the dihydrate process. The capital costs and production costs are higher than in the dihydrate process (Ghafoori and Chang, 1993). However, the higher costs are somewhat balanced by the purity of the acid and the savings in energy.

The dihydrate ($CaSO_4 \cdot 2H_2O$) process, which is used most commonly all over the world, is said to produce 28% to 30% pure acid (Ghafoori and Chang, 1993). It requires a relatively low capital cost, has a relatively low production cost and allows flexibility in the quality of phosphate rock used. This method is capable of producing an acid from which uranium can be extracted. The phosphogypsum produced cannot be used either for the wallboard or for the cement industry without prior pretreatment. It requires washing, lime neutralization, calcination and granulation to assist solid handling and feeding of the cement kiln.

The hemidihydrate procedure combines the advantages of the dihydrate process with the requirement for clean gypsum residue as produced by the hemihydrate method (Ghafoori and Chang, 1993). This process produces 40% to 52% pure phosphoric acid. The phosphogypsum produced requires lime washing, granulation and calcination treatments because of the dihydrate nature. This method is used least frequently because of its higher capital investment, production, and maintenance costs.

1.2.2 Impurities in phosphogypsum

Phosphogypsum is acidic due to residual phosphoric acid, sulphuric acid and fluorides within the porosity (Rutherford et. al., 1994). For example, the authors found that the pH of extracts from Florida phosphogypsum ranged between 2.1 and 5.5. The acidic nature of fresh phosphogypsum may keep trace elements which have been dissolved from the phosphate rock in a potentially mobile state. Among the concomitant impurities are fluorides, sulphates, acids, organics, and naturally occurring radionuclides (U and Cd etc.) (Rutherford et. al., 1994).

The type and quantity of impurities in individual phosphogypsums depend mainly on the raw phosphate, on the phosphoric acid process and on the quality of the washing in the phosphoric acid filter (Wirsching, 1978). Igneous raw phosphates produce a gypsum that is free of organic impurities. Sedimentary raw phosphates contain organic contaminants. Even the inorganic impurities of the raw phosphates reappear partly in the gypsum. The influence of the phosphoric acid process (dihydrate, hemihydrate or hemidihydrate) was discussed in detail in Section 1.2.1.

Impurities in phosphogypsum emanate largely from reaction products in the wet process and the raw material (phosphate rock) (Rutherford et. al., 1994). It is very difficult to classify phosphogypsums from plant to plant because of the variations in raw material, operating conditions (sulphuric acid concentration, temperature of acidulation, oxidation conditions, amount of sulphuric acid and so on) and because of the fluctuations in the climatic conditions under which they are stored (Gadalla et. al., 1987).

A large proportion of the impurities is found on (1) the surface of gypsum crystals, and (2) in the interstice of agglomerated crystals (Ölmez and Erdem, 1989). Impurities that adhere to the surface of the gypsum crystals include, among others, free phosphoric acid, phosphates, sodium hexafluorosilicate, sodium sulphate, fluorosilicic acid and organics. Impurities that are substituted in the crystal lattice of gypsum include calcium hydrogen phosphate, monosodium phosphate and fluorophosphates. HPO_4^{2-} may substitute SO_4^{2-} in gypsum, because of similar lattice parameters, to form a solid solution of gypsum with calcium hydrogen phosphate dihydrate ($CaSO_4{\cdot}2H_2O$-$CaHPO_4{\cdot}2H_2O$).

Singh and Garg grouped the fluoride impurities into three types (Singh and Garg, 2000), namely:

- water-soluble: a large portion of F exists as NaF and Na_2SiF_6 on the surface of gypsum crystals and in the interstices of agglomerated crystals,

- a portion of F in the gypsum lattice which has entered into solution with gypsum by substitution of FPO_3^{2-} and AlF_5^{2-} ions for SO_4^{2-}, because these crystals have an identical lattice parameter and belong to the analogous space group and,
- insoluble form as CaF_2.

The concentration of impurities in the process water is high, for example, in the Togo (Africa) phosphate rock, a high concentration of 6070 mg/*l* fluoride was obtained (Rutherford et. al., 1995). It is this residual process water in the pores of freshly deposited phosphogypsum that is a potential source of groundwater contamination if the residual water moves down below the phosphogypsum repositories.

Fluoride is a species of environmental concern and is regulated in the water supply. In the domestic water supply as well as in the industrial supply used in the food and beverages industries, fluoride concentrations should not exceed the required levels. According to the South African Water Quality Guidelines, the current fluoride Target Water Quality Range (TWQR) was ≤0.75 mg/*l* (SA Water Quality Guidelines, 1996). However, the South African Drinking Water standard has been revised to 1.5 mg/*l* (Coetzee et. al, 2003).

Typical levels of fluoride are (SA Water Quality Guidelines, 1996):

- 0.1 mg/*l* in unpolluted surface water.
- 3 mg/*l* in groundwater, but as a consequence of leaching from fluoride containing minerals to groundwater the levels rise substantially in certain cases. However, recent studies indicate fluoride levels in the range 1 mg/*l* up to as high as 30 mg/*l* in certain parts of the North West Province in South

Africa (Coetzee et. al, 2003).

- Sea water contains approximately 1.4 mg/*l*.

Radioactivity in phosphate rock is said to originate from the U-238 and Th-232 decay series (Rutherford et. al, 1994). Figures 1.1 and 1.2 show both these series. In each figure, diagonal arrows indicate beta-decay and vertical arrows indicate alpha-decay. Radionuclide half-lives are included.

Figure 1.1: U-238 decay series (Rutherford et. al., 1994).

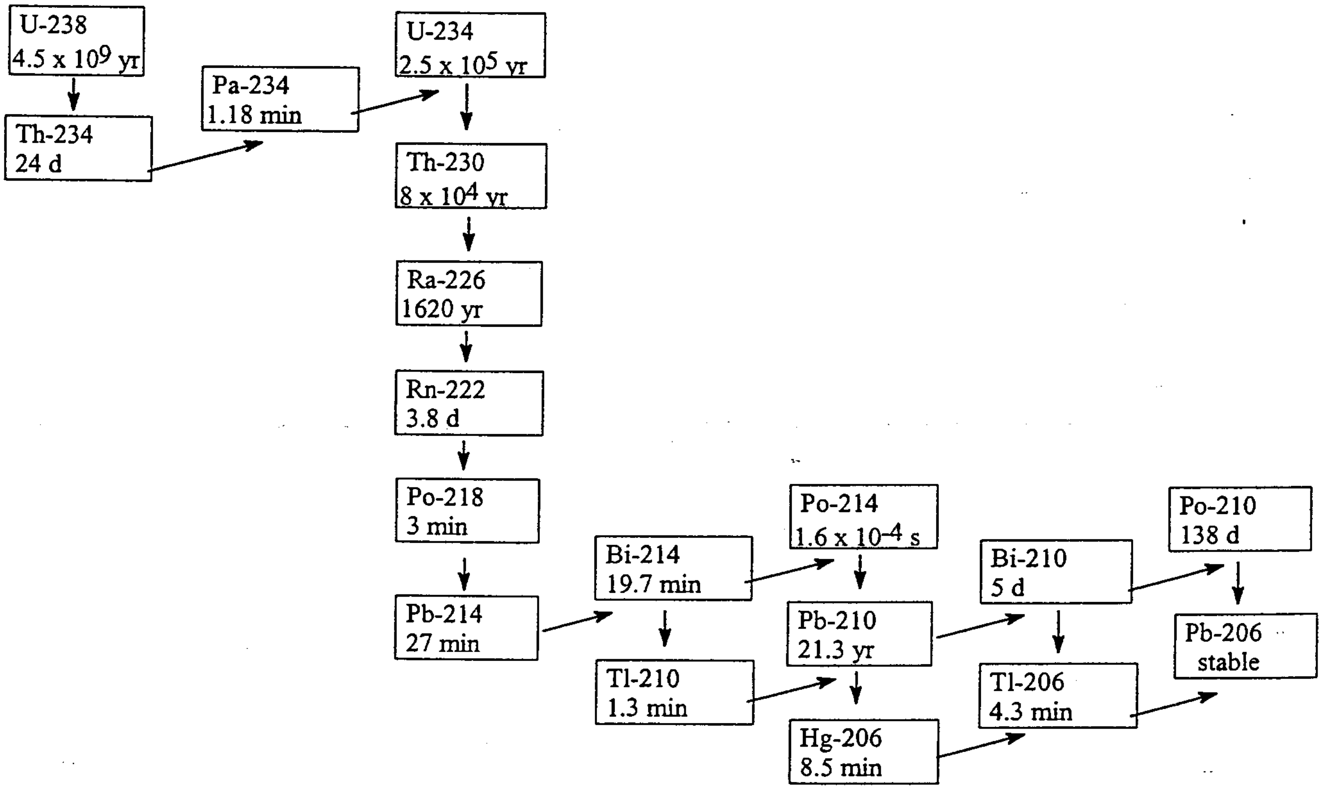
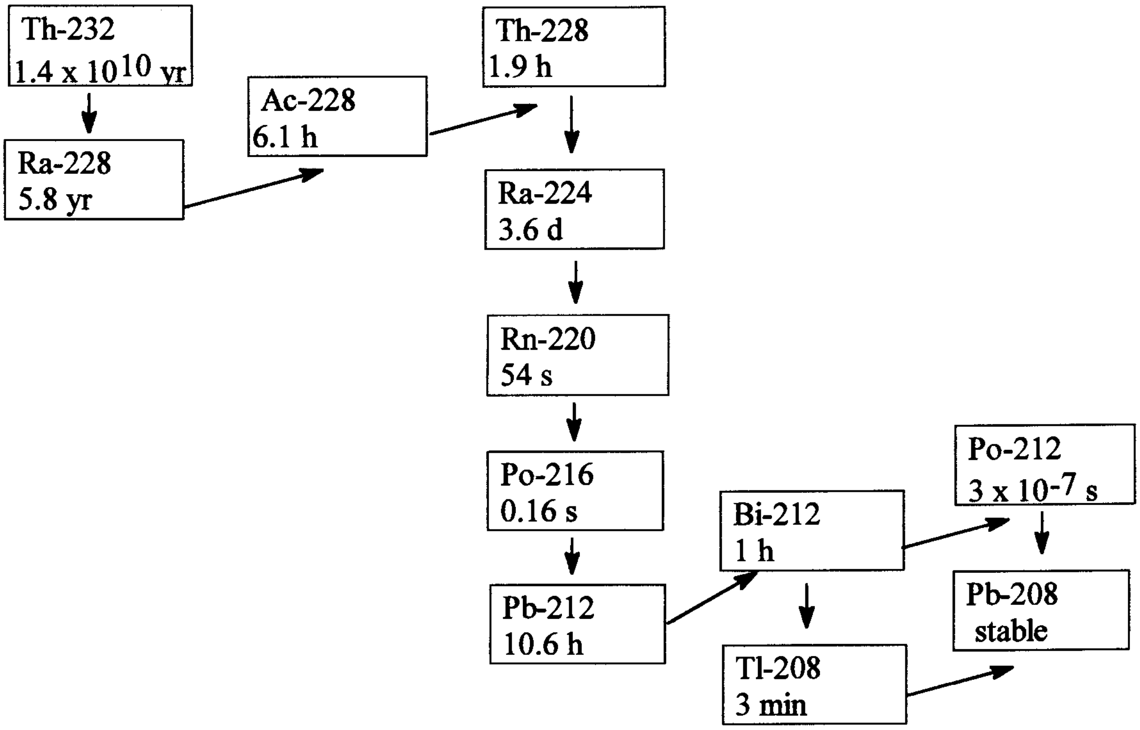


Figure 1.2: Thorium-232 decay series (Rutherford et. al., 1994)



Uranium as U(IV), with ionic radius(IR) = 0.097nm, replaces Ca in the apatite structure. Some U(VI) may be adsorbed as the uranyl ion (UO_2^{2+}) onto the apatite crystal surfaces (Rutherford et. al., 1994). Thorium as Th(IV) is thought to substitute for Ca in the apatite structure due to similarity of the two ionic radii (0.102 and 0.099 nm, for Th and Ca respectively) (Rutherford et. al., 1994).

Phosphate ores are of different quality and wide compositional variation. Rutherford et. al., mention that the majority components in phosphates rock concentrates from a variety of sources are: CaO (29-54%), P_2O_5 (24-40%), SiO_2 (0.1-14%), F (1.3-4.1%), CO_2 (0.2-7.3%), SO_3 (0.0-3.3%), Al_2O_3 (0.2-1.8%), Fe_2O_3 (0.1-2.6%), MgO (0.0-2.2%) and Na_2O (0.2-1.5%) (Rutherford et. al., 1994).

Fluoride in phosphogypsum has been said to be one of the impurities that negatively affects the use of phosphogypsum as a cement setting retarder (Japanese Patent, 1972). Singh et. al. mention that various impurities, including fluoride, in phosphogypsum used for cement manufacture and plasters tend to impair the mechanical properties by modifying the morphology of the hardened gypsum (Singh et. al., 1993). It is suggested that some of the impurities (fluoride, phosphates, etc.) in phosphogypsum form a protective coating (CaF_2 and $Ca_3(PO_4)_2$,etc.) on the surface of the cement particles, thus suppressing their hydration. Murakami states that the liquid phase in paste of Portland cement has a generally high pH value due to the high concentrations of lime and alkali (Murakami, 1968). Deprotonation of acidic phosphate species can lead to deposition of basic, insoluble tricalcium phosphate on the surface of the cement grain, providing a protective barrier against attack by water (Tabikh and Miller, 1971). Similarly, soluble fluoride such as sodium fluoride yields ions in solution that can precipitate as calcium fluoride in the high-lime region surrounding the grain.

The proposed mechanism of the action of the more complex species such as Na_2SiF_6 and $CaH_2P_2O_7$ is given as (Tabikh and Miller, 1971; Mukarami 1968):

$$SiF_6^{2-} + 6OH^- \rightarrow 6F^- + SiO_3^{2-} + 3H_2O$$

$$2F^- + Ca^{2+} \rightarrow CaF_2$$

and

$$H_2PO_7^{2-} + 4OH^- \rightarrow 2PO_4^{3-} + 3H_2O$$

$2PO_4^{3-} + 3Ca^{2+} \rightarrow Ca_3(PO_4)_2$

It has been further suggested that the second portion of the retardation action by the above complex species may be attributable to the ability to serve as "bridges" or "cross-linking agents" between hydrating grains, or quasi "bidentate ligands" on one grain, through -Si-O-Si or -Si-O-P-O-Si linkages. These structures, which involve chemical bonding, should form a more rigid and ordered protective "zone" than a simple depositional covering (Tabikh and Miller, 1971).

Unfortunately, untreated phosphogypsum cannot be used in the cement industry due to the level of impurities which has a detrimental effect on the cement setting retarder. Concentrations of impurities in phosphogypsum may differ between phosphate plants, depending on the type of phosphate rock used in chemical processing and on the temperature, redox conditions and chemical composition within the sulphuric acid digester. Phosphogypsum produced by the dihydrate process has the highest concentration of impurities (Rutherford et. al., 1994). These impurities are mainly fluorine compounds (1.5-2.5%) and phosphate compounds (0.82% by weight). Filter cakes from the dihydrate process may contain as much as 0.5-1.0% P_2O_5 (Rutherford et. al., 1994).

1.2.3 Uses of phosphogypsum

A very large proportion of waste gypsum is made up of phosphogypsum which is produced in large amounts during phosphoric acid production. The annual world production of this material was estimated at 300 million tonnes for the year 2000 (Friedhelm et. al., 1987).

Phosphogypsum is generally used in those cases where it can substitute natural gypsum. However, phosphogypsum use can be expensive since it may have to be purified in order to meet the requirements of the particular application. If there are no deposits of natural gypsum or if the natural gypsum reserves are insufficient in a particular country, however, it may in fact be more economical to use phosphogypsum.

Gypsum is a basic raw material in the manufacture of various building materials. It is used for the production of gypsum plaster and shaped products, in the form of panels or plaster boards etc. In the cement industry, gypsum is used as a set retarder.

The manufacture of Portland cement begins with the identification of the required rock deposits; primary limestone or secondary limestone, clays or shales (Mandel, 1991). The rock is quarried and then transported to a crushing plant. The weighed portions of limestone, clay and iron oxide are mixed and fed into the raw mill where the mixture is ground to a fine powder. The mixture is carefully stored in a blending silo, ensuring that it will have the correct average composition. The material is then fed into a kiln where it is swept by hot gases into a number of cyclones. The temperature of the material entering the kiln is usually in the order of 900 – 1000°C. At this temperature all the moisture, both free and inherent, is removed from the feed, and the chemical reactions begin. In the first instance, the calcium carbonate and any magnesium carbonate splits into calcium oxide, magnesium oxide and carbon dioxide. The latter leaves the system together with the combustion gases. As the temperature increases, the alumina and iron oxide start to react with calcium oxide to form calcium aluminates (mainly C_3A, tri-calcium aluminate) and calcium alumino ferrite (C_4AF). The melt of these compounds reacts with solid calcium oxide and solid silica to form dicalcium silicate (C_2S) which may convert to tri-calcium silicate (C_3S) in the presence of excess calcium oxide.

The final silicate reactions take place in the burning zone at temperatures as high as 1450 – 1500 °C. The material leaving the kiln, called clinker, is cooled. The clinker is finely ground and mixed with approximately 5% gypsum. The purpose of the gypsum is to slow down the setting of the cement when it is mixed with an adequate amount of water. The cement is then packaged and stored in warehouses.

Taylor defines the term "setting" as stiffening without significant development of compressive strength, and it typically occurs within a few hours (Taylor, 1997). If too little gypsum is added, or none at all, many cements undergo "flash" or "quick" set (Taylor, 1997). This is a rapid set, with much evolution of heat; plasticity is not regained on continued mixing, and the subsequent development of strength is poor.

When water is added to Portland cement, it initially reacts with tri-calcium aluminate (C_3A) (Mandel, 1991). Flash set may be the result. When gypsum ($CaSO_4{\cdot}2H_2O$) is present some of this dissolves in the water and reacts with the hydration products of the C_3A, forming an insoluble calcium sulpho-aluminate hydrate called ettringite ($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$). As an explanation of the set control, it is visualised that the ettringite forms a skin around the individual C_3A crystals, but as it is formed it tends to trap water between itself and the C_3A. The water reacts with the C_3A causing an increase in volume. This results in the bursting of the skin but again the trapping of some water. In this way the hydration of the C_3A is controlled, giving the user the chance to work with the cement before it sets. If the gypsum was not added to the cement, the whole mix would turn into an unworkable mass, as the reaction between water and C_3A is instantaneous.

Setting times are commonly measured empirically, using the Vicat needle. In this device, weighted needles of standard design are allowed to sink into the paste, and the initial and final setting times, defined as the times when the degree of penetration falls below the specified levels, are measured. In the British standard, the initial set must occur not earlier than 60 minutes (45 minutes for the highest strength classes) (Taylor, 1997).

Japan does not have an abundance of natural gypsum (Murakami, 1968). Phosphogypsum has therefore been used as a valuable source of raw material for controlling setting time of Portland cement, producing gypsum boards, and production of gypsum plaster. The phosphogypsum is treated to reduce the levels of soluble impurities such as phosphates and fluorides before it is used as cement setting retarder (Takemoto et. al., 1957 and Takemoto et. al., 1958). Kobayashi showed that the water soluble impurities, in the form of monocalcium phosphate, calcium hydrogen phosphate and sodium silicofluoride, markedly retarded the setting of paste in proportion to the amount of reagent in the cement. However, it was observed that the three day strength of mortar was not affected even at relatively higher concentrations of each impurity (Kobayashi, 1963).

Various researchers have been working on the use of phosphogypsum in order to tap into this highly available resource. Beretka et. al. undertook studies which revealed that there was a potential for use of chemical gypsum as a raw material for the manufacture of calcium sulphoaluminate cements. They noted that only about 4% of gypsum is required in the manufacture of Portland cement as opposed to about 30% in calcium sulphoaluminate cement manufacture (Beretka et. al., 1996).

The Russian researchers, Èminov et. al.(1989), wrote about the use of thermal phosphogypsum slag in the production of ceramic tiles. Their method was based on reprocessing phosphogypsum material to convert it into thermal phosphogypsum slag using ash from Angrensk Power Station (Russia) and coal. The firing was done in a rotary kiln at 1200 °C.

In Polk County, Florida, phosphogypsum has been used in the construction of pavement and experimental roads (Ghafoori and Chang, 1993). When the local groundwater was subjected to environmental monitoring, the results did not indicate any measurable influence of phosphogypsum impurities on the water quality of the sites. Nanni and Chang (1989) reported on the use of phosphogypsum in the construction of parking facilities at the Florida Institute of Phosphate Research. The phosphogypsum provided a good mix compactability and surface finish because of its fine grading and it was not detrimental to the strength of the roller compacted concrete.

Of all the sulphur used as sulphuric acid in the fertilizer industry in Brazil, approximately 68% is retained as phosphogypsum (de Freitas and Albuquerque, 1991). Since Brazil's sulphur market moves around 1.5 million tonnes, 80% of which is imported, recycling of phosphogypsum is strategically important. Sulphur is recovered from phosphogypsum by the Merseberg process (de Freitas and Albuquerque, 1991). In this process, phosphogypsum is purified and then reacted with carbon dioxide in its liquid state to form ammonium sulphate and calcium carbonate. The disadvantage is that in the fertilizer industry, ammonium nitrate and urea are preferred as sources of nitrogen since they yield higher concentrations of nitrogen than ammonium sulphate.

Sulphuric acid can be produced from phosphogypsum by reaction with coke and clay at temperatures of between 900–1100 °C (de Freitas and Albuquerque, 1991). The reaction products are CaO and SO_2. The clay reacts with $CaSO_4$ and CaO to produce cement clinker and the SO_2 is sent to a sulphuric acid plant.

Elemental sulphur can be removed from phosphogypsum by reduction to CaS at 1000 °C. The CaS is hydrolyzed with water in the presence of CO_2 to produce $CaCO_3$ and H_2S. The H_2S is converted to elemental sulphur in a conventional Claus sulphur recovery plant (de Freitas and Albuquerque, 1991).

Morocco is the third largest producer of phosphate in the world (Sebbahi et. al., 1997). Moroccan industry produces phosphoric acid by the sulphuric acid process because of the ease with which the products are separated by filtering. However, Morocco does not have the necessary conventional sulphur resources and, hence, imports 100% of their sulphur needs. Morocco therefore finds the salvage of sulphur from phosphogypsum an attractive option (Sebbahi et. al., 1997).

In the biotechnological route, sulphate reducing bacteria can be used in the production of hydrogen sulphide from calcium sulphate. The limitations of this method lie in the selection of suitable organic substrates which are rich in carbon but inexpensive enough to be economical (de Freitas and Albuquerque, 1991).

Roy et. al. investigated the application of phosphogypsum as aggregate material in concrete (Roy et. al., 1994). Aggregates can be used in Portland cement provided that there is no reaction with cement and that chemical reactions that do occur do not cause high volume changes. Phosphogypsum, pyrite, phosphatic clays, petroleum coke and sand (silica) were heated to high temperatures (ca. 1300 °C). The sulphur was recovered as SO_2 leaving a solid residue. This residue was used as aggregates in concrete. The treatment of the residue prior to its use entailed burning it to reduce the sulphate levels to approximately 4.5%. At these levels, the residue was not found to be detrimental when used as aggregates in Portland cement (Roy et. al., 1994).

Phosphogypsum can be used as an important source of rare earth elements (Jarosiński et. al.,1993). The rare earth content of phosphogypsum depends on the conditions of product decomposition. If phosphoric acid production is carried out by the dihydrate method, about 70% of the rare earth concentrates are taken up in the structure of the phosphogypsum and the rest remain in the phosphoric acid. If the process is carried out by the hemihydrate method, the rare earths are taken up almost entirely in the waste product. Jarosiński et. al. developed a modified wasteless process of apatite phosphogypsum utilization which could be applied to both the hemihydrate and the dihydrate phosphogypsums. In this process, the rare earth elements, phosphates, fluorides etc. are leached with sulphuric acid of between 10 and 40 % concentration.

There are various agricultural uses of chemical gypsum. Firstly, it is used to reduce high levels of soluble aluminium and to supply calcium to some subsoils, mainly in tropical and sub-tropical soil types. This allows deeper root penetration by crops in the soil, thus providing better water and nutrient extraction (de Freitas and Albuquerque, 1991). Secondly, phosphogypsum may be used as a source of sulphur in sulphur deficient soils (de Freitas and Albuquerque, 1991). The third and most important common use of phosphogypsum is in the combatting of alkalinity and salinity in soils that have a high sodium concentration. Sodium in soils tends to be retained in clay and phosphogypsum allows the displacement of sodium by calcium, reducing the alkalinity (de Freitas and Albuquerque, 1991 and Wirsching 1978).

One important factor in the use of phosphogypsum in agricultural soil is the possibility of raising the overall radioactivity of the soil such that it becomes unsuitable for other uses. Even though the land may continue to be used for agricultural purposes, it may become unsuitable for residential use due to the potential radon risk indoors and direct gamma radiation (Rutherford et. al., 1994).

1.3 Removal of fluoride impurities from phosphogypsum

The amount of phosphogypsum generated worldwide per annum is approximately 150 million tons, 50% more than the consumption of natural gypsum; on average, its utilization rate does not exceed 15% (Beretka et. al., 1996). Calcium sulphate dihydrate, which is the most frequent phase in chemical gypsum, is used mainly as a set retarder in the cement industry and as a raw material for the manufacture of plaster and preformed building elements. It must be taken into account that, in all the above mentioned applications, some impurities present in several chemical gypsums can influence the characteristics of commercial products considerably (Beretka et. al., 1996). In the sections that follow various methods of removing fluoride impurities from phosphogypsum will be discussed.

1.3.1 Diluted ammonium hydroxide treatment

Various methods for reducing the impurities in phosphogypsum have been suggested. Phosphogypsum has been purified by washing with NH_4OH (aq) (10-20%) to convert phosphatic and fluoride impurities to water soluble ammoniated compounds (Singh et. al., 1993). The treated phosphogypsum was subsequently washed with water. It was observed that the strength of cement made with purified phosphogypsum, instead of natural gypsum, increased relative to that made with unprocessed phosphogypsum. The researchers mentioned that this treatment would be useful in removing organic as well as inorganic impurities.

1.3.2 Water wash, lime wash and thermal treatment

Smadi et. al.(1999) purified the phosphogypsum by washing the sample with water and then by calcining at various temperatures (170 °C to 950 °C). It was observed that the total amount of fluoride in unwashed phosphogypsum decreased progressively from 2.12% (170°C) to 0.16% (950°C). In the case of the water-washed sample, the total fluoride decreased progressively from 0.89% (170°C) to 0.27% (950°C).

Ölmez and Erdem mention that the impurities can be removed by washing with water, milk of lime and treating with milk of lime after calcination. Only water soluble impurities can be removed by washing with water and milk of lime. Calcium hydrogen phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$) forms a solid solution with gypsum and pure $CaSO_4{\cdot}2H_2O$ because of similar crystalline parameters. Calcination converts the phosphogypsum to the hemihydrate form ($CaSO_4{\cdot}1/2H_2O$) to remove these HPO_4^{2-} ions. The hemihydrate, having a different crystal structure to calcium hydrogen phosphate, cannot form a solid solution with $CaHPO_4{\cdot}2H_2O$. The phosphate passes to the solution and is converted to inactive compounds, such as $Ca_3(PO_4)_2$, by means of a reaction with milk of lime (Ölmez and Erdem, 1989).

Impurities such as phosphates and fluoride can be removed by treatment of the phosphogypsum with lime water or aqueous cement extracts (Tabikh and Miller, 1971). This converts acidic phosphates into $Ca_3(PO_4)_2$ and complex fluoroanions into CaF_2, insoluble silicates and aluminates.

Erdogan (1994) studied the effect of impurities on the setting time of paste containing untreated phosphogypsum or borogypsum (chemical gypsum obtained as a coproduct in boric acid manufacture). It was observed that the setting time of cement containing borogypsum was retarded by the presence of the orthoboric acid impurity. The study also showed that the setting time of Portland cement paste containing untreated phosphogypsum was markedly retarded. The initial and final setting times of phosphogypsum mixes decreased considerably due to the inactivation of all water soluble impurities by milk of lime. It was therefore recommended that phosphogypsum that is to be used to control the setting of Portland cement should be washed with lime milk.

1.3.3 Diluted sulphuric acid treatment

Jarosiński (1994) described a method in which he leached the phosphogypsum sample in a 12% (mass percentage) sulphuric acid solution to recover rare earth elements, and then converted it into anhydrite II (insoluble Calsium sulphate unhydrite) in a 50% sulphuric acid solution. The procedure is summarised in Table 1.1.

Table 1.1: Experimental conditions followed by Jarosiński to purify and recrystallize anhydrite phosphogypsum (Jarosiński, 1994).

	Stage:	
Parameters	**Leaching**	**Conversion**
Temperature	40°C	50°C
Sulphuric acid concentration (mass %)	12%	50%
Solid/liquid mass ratio	1 : 2	1 :1
Time of process	45 min	120 min
Standardized mechanical agitation, revolution	150 min^{-1}	150 min^{-1}

Jarosiński found this method to be successful in removing some of the undesirable impurities, such as phosphorous, fluorine and sodium. The amount of fluoride was initially reduced from a total of 0.39 % (m/m) to 0.04% after leaching with the 12% sulphuric acid, and eventually to 0.00% in the anhydrite. Recrystallization of phosphogypsum into anhydrite II made the recovery of rare earth elements possible, and the species that are adsorbed both on the surface and in the crystal lattice of crystals could also be substituted. The following equilibrium process takes place during the conversion:

$$H_2SO_4\,(aq) + Ca(H_2PO_4)_2\,(s) \rightleftharpoons CaSO_4\,(s) + 2H_3PO_4\,(aq).$$

Jarosiński suggests a reduction of the levels of phosphate and fluorine to about 0.8% and 0.2% respectively before the phosphogypsum can be used as substitute for natural gypsum.

A method of purification of apatite phosphogypsum was developed in Poland to recover rare earth elements (Jarosiński et. al., 1993). The method applies to both dihydrate phosphogypsum taken from the stacks and the hemihydrate phosphogypsum. The phosphogypsum is leached with sulphuric acid with an optimum concentration of not more than 10% at temperatures lower than ambient (0-10°C). During the process of leaching, phosphates, fluorides, rare earths and other elements contained in the phosphogypsum pass into the leaching acid. The purified phosphogypsum is used for production of β-hemihydrate (plaster of Paris) by the thermal method and as anhydrite cement.

A good number of phosphogypsum purification methods have been patented in various countries. Some of these methods are discussed in the following sections.

1.3.4 Patented method: Fluorine volatilization

The British patent 284701 explains the method of defluorination of phosphogypsum for the production of sulphuric acid and cement clinker. In this case, gypsum is mixed with finely divided silica and calcined between 200 and 400°C in a stream of water vapour. The ratio of silica to fluorine in the gypsum should be 2 (by mass). It is claimed that fluorine will be effectively removed in this way.

1.3.5 Patented method: Thermal treatment of impurities in solid solution

The Japanese patent number 1966-54968 discusses a method for the elimination of impurities, such as phosphate and fluorine compounds, adsorbed or present in solid solution in phosphogypsum. In this patent, calcium phosphate or fluorine compounds are "removed" by calcining the by-product gypsum at a temperature between 120 and 250 °C. Under these conditions, calcium sulphate hemihydrate, or a mixture thereof with soluble anhydrous gypsum, is obtained. When this is rehydrated with sulphuric acid, the calcium phosphate or fluorine compounds present in the solid solution prior to recrystallization of the gypsum dissolve in the sulphuric acid and do not return to the solid solution state, evidently eliminating these impurities. The improved gypsum always contains less than 0.3% phosphate (P_2O_5) and less than 0.02% fluorine compounds (F). When the purified compound is used in cement, it is found to approach the properties of high quality foreign natural gypsum. In the abovementioned patent it is stated that some of the methods used previously to eliminate impurities to improve the quality of by-product gypsum include:

- washing by-product gypsum with water,
- washing by-product gypsum with milk of lime, and
- calcining the by-product gypsum to produce the hemihydrate or a mixture thereof with soluble, anhydrous gypsum and following this up with hydration treatment with unslaked lime or other alkaline substances.

It was stated, however, that the fluorine compounds are not totally eliminated after treating the by-product gypsum with any of the three methods mentioned (Japanese patent number 1966-54968).

1.4 Disposal of phosphogypsum

Phosphogypsum is disposed of primarily on land or by pumping it into rivers or the sea. Almost 58% of phosphogypsum produced worldwide is stockpiled on land, about 28% is discharged into the ocean and the remainder is reprocessed and utilized (Ghafoori and Chang, 1993). The United States Environmental Protection Agency, as stated in the US Federal Register 1990, requires that all phosphogypsum be placed in stacks or mines (Rutherford et. al., 1994).

On land, phosphogypsum can be disposed of dry or wet. Wet disposal is done by slurrying and pumping the phosphogypsum filter cake with process water to a sedimentation pond where it is settled. This procedure is also referred to as wet stacking. The overflowing process water is circulated for re-use or sent to water treatment plants. In dry disposal or dry stacking the filter cake is taken by truck or transported on conveyor belts to disposal facilities where it is stacked (Ghafoori and Chang, 1993).

In the wet phosphoric acid process industry, the process water is recirculated. The concentration of water soluble impurities, such as fluoride, may increase as this recirculation occurs. Disposal of phosphogypsum on land may pose seepage problems beneath the repositories or the process water holding ponds. The fluoride may then attack silicate minerals and dissolve them, according to the equation,

$$H_2O + HF + MAlSiO_2 \rightleftharpoons M^+ + AlF_2^+(4H_2O) + SiF_4 + n\,H_2O$$

where $MAlSiO_2$ represents an aluminosilicate mineral, M represents Ca, Mg, Na, K, and Fe, and $AlF_2^+(4H_2O)$ is a complex ion of Al (Rutherford et. al., 1994). Some of the SiF_4 may hydrolyze to form H_2SiF_6 within the phosphogypsum leachates. The presence of clay soil at the bottom of the phosphogypsum repository may result in dissolution of clay which may allow movement of contaminants into the groundwater to become accelerated over time.

Morris, however, provides comprehensive information regarding the construction of a phosphate fertilizer facility that has major environmental improvements (Morris, 1993). In this case, all containment systems are designed to contain and control any potentially released material in order to avoid contact with the environment. The systems include audio and visual warning alarms. In order to protect groundwater, the first line of protection is a two-tiered clay liner. A system of pipes is used for collection of process water to a holding area. The entire field is surrounded by a wall composed of a mixture of on-site clays and bentonite clay which forms a low permeability barrier. The wall extends deep into the underlying clay to ensure that any process water that reaches the edge of the field cannot escape under the wall.

1.5 Environmental concerns related to the storage of phosphogypsum

Contamination of the environment from stored phosphogypsum may occur from sources such as:

- atmospheric contamination by fluoride or other toxic elements,
- ground water pollution from mobile ions,
- radon gas, inhalation of radioactive dust and direct exposure to gamma radiation. (Rutherford et. al., 1994)

1.5.1 Atmospheric pollution from fluoride

Atmospheric contamination occurs from fluoride gas emissions from stacks, and from transport of fine dust particles containing fluoride. Fluoride gas emission occurs mainly from operational stacks while the transport of fine dust particles is of concern in both operational and inactive stacks. Fluoride volatility emanates from the formation of HF and SiF_4 during processing. Most plants use scrubbing to remove fluoride so that the fluoride emissions from stacks are reduced to a very low minimum.

1.5.2 Groundwater contamination

Groundwater contamination occurs due to the seepage that results from rainwater leaching through stacks. Process water is acidic and thus has a high potential to mobilize various elements (As, Cd, Cr, Pb, Na, F^-, Mn, Fe, SO_4^{2-}, U and Th) solubilized from the phosphate rock acidulation process. High levels of these species, which are beyond the set limits for drinking water regulations, could pose health problems (Rutherford et. al., 1994).

1.5.3 Radon gas and other radioactive species pollution

Exposure to Rn-222 is one of the greatest concerns as high doses may cause lung cancer. In-depth studies conducted in areas near phosphogypsum stacks in Florida found that the concentrations of radon were generally very low and hence posed no health risk (Rutheford et. al., 1994). The combination of the presence of heavy metals such as lead, and the radionuclides from the ^{238}U and the ^{232}Th decay series in phosphate ore, the large amounts of ore processed in the phosphate fertilizer industry and the incorporation of heavy metals and radionuclides into the gypsum matrix, give rise to concern about the environmental impact of the emission of phosphogypsum (Sloof et. al., 1996). Hence, it is recommended that for each phosphogypsum stack, the levels of radioactivity be studied in order to determine the site specific environmental health risk.

1.6 South African Chemical Gypsum

South African chemical gypsums under consideration in this study are titangypsum and phosphogypsum. Titangypsum is produced as a co-product at a titanium dioxide production plant. Phosphogypsum, as discussed in Section 1.2, is produced as a by-product by various phosphate fertilizer plants. Titangypsum is a co-product, as opposed to a by-product, because it is specifically manufactured at a separate plant after the production of the titanium dioxide.

1.6.1 Titangypsum

Titangypsum has been defined as a type of chemical gypsum co-produced during the manufacture of titanium dioxide white pigment (Murakami, 1968). Titanium white, TiO_2, is produced by sulphuric acid reaction with an ore such as ilmenite ($FeTiO_3$). The simplified reactions for the production of this chemical gypsum are

$$FeOTiO_2(s) + 2\ H_2SO_4(aq) \rightarrow TiOSO_4(s) + FeSO_4\ (aq) + 2H_2O(l)$$
$$TiOSO_4(s) + 2H_2O(l) \rightarrow TiO(OH)_2(s) + H_2SO_4(aq)$$
$$FeSO_4\ (aq)/\ H_2SO_4\ (aq) + CaCO_3\ (s)/\ Ca(OH)_2(s) \rightarrow CaSO_4{\cdot}2H_2O(s).$$

The principal impurities present in titangypsum are iron(III) hydrogel, $Fe_2O_3{\cdot}xH_2O$, and crystalline hydrated iron(II) sulphate, as well as some remaining unreacted titaniferrous ore (Bensted, 1981). These iron compounds impart a brown colour to the titangypsum which could give rise to aesthetic problems when used for production of certain types of Portland cements.

Titangypsum has shown itself to be an effective setting modifier and an adequate substitute for the natural gypsum used hitherto in the production of Portland and slag-Portland cement (Bensted, 1981).

The main sources of impurities are the raw materials and the manufacturing process. The application and treatment of this chemical gypsum are similar to those discussed above for phosphogypsum.

1.6.2 Others

Phosphate rock deposits in South Africa are confined to igneous and marine sedimentary geological environments (Roux et. al.,1989). About 95% of South African phosphate production is derived from the igneous type. The marine sedimentary deposits occur both onshore and offshore along the southern coast from Port Elizabeth in the Eastern Cape Province, stretching to Lamberts Bay to the north of Cape Town in the Western Cape Province. The igneous phosphate deposits in South Africa are mainly derived from the Phalaborwa Complex, situated in the Limpopo Province (Coetzee et. al., 1976 and Roux et. al., 1989).

The average chemical analyses of representative rock samples across the entire Phalaborwa Complex show a fluoride (F) content of 0.24% (apatite rich massive pyroxenite), 0.01% (apatite poor massive pyroxenite), 0.38% (apatite rich phlogopite pyroxenite), and 0.78% (apatite rich glimmerite) (Fourie and De Jager, 1986). The fluoride content of other rock types was too low to be detected. However, it should be emphasized that continuous rock bodies with these compositions do not exist. Rather, the rocks exist as mixtures characterized by the predominance of a certain rock type.

The phosphate rock produced at Phalaborwa Complex is attractive to both the domestic and the export market because:

- it has a high P_2O_5 content (which is advantageous in superphosphate fertilizer production),
- it is low in CaO content (which reduces the acidulation costs during fertilizer production) and,
- it has a low content of deleterious impurities such as iron, carbon dioxide, arsenic, lead, mercury, cadmium and organic carbon. (Roux et. al, 1989)

South Africa has vast reserves of natural gypsum dispersed through all the provinces (Brabers, 1976). This material is mainly used in the cement industry as a set retarder. Chemical gypsum is formed as a by-product during the manufacture of superphosphate fertilizers and also from various other South African industries. For every ton of superphosphate, four to five tonnes of chemical gypsum are produced (Brabers, 1976). The high production of chemical gypsum necessitates research on how best to dispose of the material in environmentally responsible ways, and how to find other possible uses for the material.

Chapter 2 Fluoride Analysis: Background

2.1 Sample preparation methods

Fluorine forms sparingly soluble compounds to varying degrees with many metal ions. Such fluoride-containing compounds are generally not easy to dissolve. Fluorine is the most reactive of all elements. Interference by other ions present in analytical procedures is considerable, either by formation of sparingly soluble fluorides or by combination with metal ions to form strong metal-fluoride complexes (Williams, 1979). Hence, it is important that some prior separation or selective complexation of the fluoride is performed or that a fluoride specific method is used to arrive at accurate quantitative results.

Fluoride may be lost during the sample preparation for material analysis due to:

- volatility of silicon tetrafluoride (SiF_4) and
- loss of HF in fumes with sulphuric acid.

The volatile silicon tetrafluoride is produced from the action of concentrated mineral acid, such as sulphuric acid, on a fluoride ore, for example the reaction of fluorspar with sulphuric acid gives

$$2CaF_2\,(s) + 2H_2SO_4\,(aq) \rightarrow 2CaSO_4\,(s) + 4HF(aq)$$

$$4HF(aq) + SiO_2\,(s) \rightarrow SiF_4\,(g) + 2H_2O(l).$$ (Bauer, 1963)

Clearly, the HF produced attacks the silica to give the volatile silicon tetrafluoride. Hence, the sample preparation methods should be designed in such a way that fluoride loss is avoided.

Generally, the classic distillation methods are based on the fact that the volatile silicon tetrafluoride is formed by the action of sulphuric acid upon a fluoride in the presence of silica. Silicon tetrafluoride is then hydrolyzed and collected as a soluble fluoride in water or alkali hydroxide. The fusion methods, using various fluxes, are used to bring fluoride into solution prior to quantitative analysis. Various researchers have used adaptations of these methods to prepare samples for fluoride analysis.

2.1.1 Fusion methods of fluoride analysis

A method of leaching out fluoride as applied to silicious ores and slags has been described (Scott, 1979). The procedure entails weighing 0.5 to 1.0 grams of material and fusing this in a crucible with ten times its weight of sodium and potassium carbonate (1:1), and then pouring the flux into an iron mould. If a porcelain crucible is used, this is broken and added to the cooled fusion. The mass is digested for an hour with about 200 mL of hot water, then boiled briskly for 10 minutes and filtered. The residue is washed with hot water, followed by a hot solution of ammonium carbonate, and the insoluble material is rejected. To remove the silica, 5 to 10 grams of ammonium carbonate are added to the alkaline solution. The solution is boiled for five minutes and allowed to stand in the cold for two to three hours. The precipitate is filtered off and washed with the ammonium carbonate solution. The fluoride passes into the filtrate, while practically all of the silicic acid remains on the filter.

Various individuals have used distillation of fluorosilicic acid in order to separate fluoride from the difficult sample matrix. For example, Grimaldi, Ingram and Cuttitta were able to eliminate the effects of silicon and aluminium in the determination of fluoride by fusion with a sodium carbonate/zinc oxide mixture followed by leaching, filtration, and distillation from phosphoric-perchloric acid mixtures (Grimaldi et. al., 1955).

Raghavan et. al.(1992) used a fusion method to bring the fluoride into solution before the analysis by Ion Selective electrodes. The solid sample is mixed with sodium hydroxide and heated in a muffle furnace at 500°C for thirty minutes, cooled, dissolved in water and filtered. The fluoride amount was determined by the ion specific electrode method.

Javellana and Jawed (1981) applied a fusion method to determine fluoride in cement and cement related materials. The sample is prepared by two fusion methods, namely fusion with $LiBO_2$ and sintering with a zinc oxide-sodium carbonate mixture. In the $LiBO_2$ method, 250 mg of the ground sample is mixed with 800 mg of anhydrous $LiBO_2$ and ignited in a muffle furnace at 1000°C for 15 minutes. The molten mass is poured into a polypropylene beaker containing about 60 mL of 4 % nitric acid and stirred with a magnetic stirrer until dissolved. The solution is transferred to a 100 mL polypropylene flask and brought up to the mark with water. In the sintering method, 100 mg of ground sample is mixed with 500 mg Na_2CO_3 and 100 mg ZnO in a platinum dish. It is then heated in a muffle furnace for 30 minutes at 900°C. The sintered mass is cooled, and 25 mL water added. The mixture is heated in a steam bath for 30 minutes. It is then filtered and the filtrate acidified with a few drops of nitric acid. It is subsequently transferred to a 100 mL polypropylene flask and brought up to the mark with water. The authors determined fluoride by the ion selective electrode method and at the same time analysed various reference materials to validate the technique.

The two sample preparation methods, namely, $LiBO_2$ fusion and zinc oxide-sodium carbonate sintering, produced identical results for most samples. The sintering method did, however, produce excellent results for samples that had high concentrations of Si, Al and Fe because these species were removed through the sintering process, and left behind as insoluble zinc silicates and aluminates. These species interfered in the $LiBO_2$ method, and the results were lower. The $LiBO_2$ method is rapid and gives excellent results for samples with relatively low SiO_2, Al_2O_3 and Fe_2O_3 contents.

Fluoride has proved to be very difficult to exchange with chloride in ores such as fluorapatite, even at temperatures as high as 600°C (Javellana and Jawed, 1981). This is because fluorine forms very strong complexes with aluminium, iron, chromium, silicon, and other trivalent and polyvalent cations. Fusion with zinc oxide-sodium carbonate eliminates or reduces these cations as explained above.

Peters and Ladd determined fluoride in various ore samples using the fusion sample preparation method as follows (Peters and Ladd, 1971):
0.5 gram of the sample is fused with 10 gram of a 1:1 Na_2O_2-Na_2CO_3 mixture in an iron crucible. The cold melt is transferred to a 250 mL distillation flask and the crucible is rinsed with perchloric acid. A quantity of 75 to 150 mg of finely ground quartz sand is added. Then 40mL of 70 % perchloric acid and 5 mL of 85 % orthophosphoric acid are added to the flask and the end of the condenser is positioned in 20 mL of water. The flask is heated until the temperature reaches 130°C, then the steam is introduced and heating continued. The temperature is held at 140–150°C, until 300 mL of the distillate has been collected. The distillate is diluted to 500 mL with water.

2.2 Fluoride Analysis methods

The experimental methods of analysis used in this study to determine the amount of fluoride in South African chemical gypsum are:

- Ion Selective electrode method,
- Ion Chromatography method and,
- Willard and Winter standard method of fluoride determination.

The background to each of these methods is briefly explained below. The Pyrohydrolysis technique has also been used by other researchers for the determination of fluoride in inorganic materials (Clement and Seargent, 1971).

2.2.1 Ion Selective Electrode method

The ion selective electrode method is a specialised technique which forms part of potentiometric methods of analysis. Potentiometric methods are based upon the measurement of potentials of electrochemical cells in the absence of appreciable currents.

The instrumental requirements for potentiometric methods include a reference electrode, an indicator electrode and a potential measuring device. A potentiometer is used to measure the signal when the electrode system is dipped into the solution under study. The results are usually given in millivolts or even directly as concentrations of the species being measured. The reference electrodes and indicator electrodes are discussed briefly below.

2.2.1.1 Reference electrodes

A reference electrode is an electrode of which the half-cell potential is known, constant, and completely insensitive to the composition of the solution under study. Typical examples of commonly used reference electrodes are the calomel electrodes and the silver/silver chloride electrodes.

2.2.1.1.1 Calomel electrodes

Calomel reference electrodes consist of mercury in contact with a solution that is saturated with mercury(I) chloride and also contains a known concentration of KCl. Schematically the calomel half-cells are represented as

$Hg \mid Hg_2Cl_2(sat'd),KCl(xM) \mid\mid$

where x is the molar concentration of KCl. The half-cell reaction for the calomel electrode is

$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$.

The electrode potential for this half-cell is dependent on the chloride concentration and the temperature of the solution. For a saturated calomel electrode, the electrode potential is 0.2444V at 25°C.

2.2.1.1.2 Silver/Silver chloride electrodes

This electrode system consists of a silver electrode immersed in a solution of potassium chloride that has been saturated with silver chloride. Schematically the electrode half-cell is represented as

$Ag \mid AgCl(sat'd),KCl(xM) \mid\mid$

where x is the molar concentration of KCl. Usually this electrode is prepared with either a saturated or a 3.5M potassium chloride solution. For a saturated silver/silver chloride electrode, the electrode potential is 0.199V at 25 °C. The half-cell reaction for the silver/silver chloride electrode is

$AgCl\,(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$.

2.2.1.2 Indicator electrodes

An ideal indicator electrode responds rapidly and reproducibly to changes in the activity of the analyte ion. There are two types of indicator electrodes, namely metallic and membrane.

2.2.1.2.1 Metallic indicator electrodes

Metallic indicator electrodes are further subdivided into:

- electrodes of the first kind (i.e. metal that is in direct equilibrium with its ions, e.g. Ag/Ag^+),
- electrodes of the second kind (a metal which is responsive to an anion with which it forms a precipitate or a stable complex ion, e.g. Ag/AgCl),
- electrodes of the third kind (a metal electrode which is made responsive to a different cation, for example, a special mercury electrode being used for determination of calcium) and,
- metallic redox indicators (e.g. $Pt/Ce^{4+},Ce^{3+}$).

2.2.1.2.2 Membrane indicator electrodes

Membrane electrodes are called ion-selective electrodes because of the high selectivity of most of these devices. The properties of ion-selective membranes include:

- minimal solubility in analyte solution,
- electrical conductivity to allow migration of charged ions within the membrane and,
- selective reactivity with the analyte.

Ion selective electrodes can be classified further into two groups, namely crystalline and noncrystalline membrane electrodes. Examples of crystalline membrane electrodes are LaF_3 for determination of F^- , and Ag_2S for determination of S^{2-} and Ag^+. Typical noncrystalline membrane electrodes are glass (silicate glasses for Na^+ and H^+) and liquid (example liquid ion exchangers for Ca^{2+}). Attention will be focussed on crystalline membrane electrodes used for the determination of fluoride since this is the aim of this study.

2.2.1.3 Fluoride Ion-Selective electrode

The fluoride electrode consists of a solid state inorganic membrane of LaF_3 crystal (Javellana and Jawed, 1981). Within this crystal lattice, fluoride is a mobile ion (free to move from one vacant site to another) whereas the lanthanum ions are in fixed lattice positions. A lattice vacancy will not accept ions other than fluoride due to differences in size, shape, or charge. Therefore, the LaF_3 membrane is highly selective for conduction of fluoride ions.

The mechanism of the development of a fluoride sensitive potential across a lanthanum fluoride is analogous to that of a glass membrane. At the two interfaces, ionization creates a charge on the membrane surface as shown by the equation

$LaF_3\,(\mathit{solid}) \rightleftharpoons LaF_2^-\,(\mathit{solid}) + F^-(\mathit{solution})$

where *solid* refers to membrane, and *solution* refers to the fluoride-containing solution outside the membrane. The magnitude of the charge is dependent upon the fluoride ion concentration of the solution. Thus the side of the membrane encountering the lower fluoride ion concentration becomes positive with respect to the other surface; it is this charge difference that provides a measure of the difference in fluoride concentration of the two solutions. The potential of a cell (at 25 °C) containing a lanthanum fluoride electrode is given by the equation (Skoog et. al., 1998):

$$E = L - 0.0592\log a_{F^-} = L + 0.0592pF \qquad \text{...2.1}$$

where pF is the negative logarithm of the fluoride ion activity (a_{F^-}) and L is a constant.

For two solutions, whose ion activities are different, the above equation may be written as

$$E_2 = L - 0.0592\log a_1 \qquad \text{...2.2}$$

and

$$E_1 = L - 0.0592\log a_2 \qquad \text{...2.3}$$

where a_1 and a_2 are the activities of solution number *1* and solution number *2* respectively. The change in voltage measurements for the two solutions may be expressed as

$$\Delta E = E_2 - E_1 = -\ 0.0592\log\frac{a_1}{a_2} \qquad \text{...2.4}$$

In order to measure the activities of a given sample solution within an analytical error of 1% for a monovalent ion, such as fluoride, the voltage measurement error may be determined from equation 2.4 as

$$\Delta E = -\ 0.0592\log\frac{100}{(100 \pm 1)} = \pm\ 0.00025V\,(0.25mV)$$

Similarly, analytical measurement errors of 0.4% and 2% would result from voltage measurement errors of ±0.1mV and ±0.5 mV respectively.

Since the reaction behaviour of ions is affected by the presence of other ions in the solution, the equation for measuring the activity of solutions with a fluoride Ion selective electrode given in equation 2.1 is usually written in terms of ion concentration as

$$E = L - 0.0592 \log \gamma_i c_i \qquad \text{...2.5}$$

where γ_i is the activity coefficient, which is a measure of the non-ideal behaviour of the solution. The activity coefficient is a function of the ionic strength as shown in equation 2.6

$$-\log \gamma_i = \frac{0.51 Z_i^2 \sqrt{\mu}}{1 + 3.3 d_i \sqrt{\mu}} \qquad \text{...2.6}$$

where z_i is the charge of the species ***i***, μ is the ionic strength of the solution and d_i is the effective diameter of the hydrated ion ***i*** in nanometers (Skoog et al., 1997). The constants 0.51 and 3.3 are applicable to aqueous solutions at 25°C. Equation 2.6 is known as the Debye Hückel equation.

A solution such as TISAB is added to both the sample and standard calibration standards in order to keep the ionic strength constant, as explained in Chapter 7. Under these conditions, the activity coefficient is constant. Hence, equation 2.5 becomes

$$\begin{aligned} E &= L - 0.0592 \log \gamma_i - 0.0592 \log c_i \\ &= L' - 0.0592 \log c_i \end{aligned} \qquad \text{...2.7}$$

Equation 2.7 shows a direct relationship between the measured voltage and the logarithm of the concentration of the measured species without necessarily knowing the activity coefficient, as was done in this study.

Most commercial fluoride electrodes can be used at temperatures between 0–80 °C. The electrodes are sensitive to pH changes. At pH higher than 8, the hydroxide ion can interfere directly with fluoride measurements. At pH values less than 5, hydronium ions interfere in total fluoride measurements; here undissociated hydrogen fluoride forms to which the electrode is not responsive (Skoog et. al, 1998).

Edmond (1969) determined fluoride in phosphate rock samples by the ion selective method. In this method, 50 mg of phosphate rock is transferred to a small polypropylene beaker. 1 mL of 5 M HCl is added to dissolve the sample. The solution is transferred to a 100 mL volumetric flask and brought up to the mark with water. This method is simple and rapid but it is adversely affected by the presence of species such as aluminium.

2.2.2 Ion Chromatographic method

Ion chromatography is an efficient method of separating and determining ionic species based on exchange equilibria between ions in solution and ions of like sign on the surface of an essentially insoluble, high molecular weight solid. Ion chromatography, as a novel analytical method, was introduced in 1975 by Small, Stevens and Baumann (Joachim Weiss, 1986).

The three separation techniques on which ion chromatography is based may be grouped as High Performance Ion Chromatography (HPIC), High Performance Ion

Chromatography Exclusion (HPICE) and Mobile Phase Ion Chromatography (MPIC) (Joachim Weiss, 1986).

- **HPIC**

This technique is based on an ion exchange process between the mobile phase and the exchange groups covalently bound to the stationary phase. For hydrophobic ions, in particular, adsorption processes are also involved. HPIC is derived from the classical column chromatography using microporous ion exchange resins. Due to the high ion exchange capacity of these resins, high eluent concentrations were necessary to ensure elution of the ions. The amount of eluent required was often several litres. Modern ion exchange chromatography utilizes ion exchange resins which are of low capacity and high efficiency. The required sample volumes are very low, allowing improved resolution due to very narrow peaks. The stationary phase is typically polystyrene based resin which has been cross linked with divinyl benzene.

- **HPICE**

This type of ion chromatography involves Donnan exclusion, steric exclusion, and adsorption processes. Ion exclusion chromatography is especially useful for separating weak organic acids from totally dissociated acids. The stationary phase is a completely sulphonated, high capacity cation exchange resin derived from polystyrene / divinyl benzene copolymer.

- **MPIC**

The primary process involved in MPIC is adsorption. The selectivity of the column is determined by the mobile phase. By adding lipophilic ions (such as alkyl sulphonic acids or quaternary aliphatic amines) to the mobile phase, solute ions with opposite charges can be separated on the common reversed phase silica columns. The stationary phase is composed of a neutral, non-polar, macroporous polystyrene/divinyl benzene based resin.

2.2.2.1 Ion Exchange Equilibria

Recently synthetic resins with functionalized exchange sites are used in ion exchange columns. The column material (resins) is synthesized to serve as cation exchange or anion exchange columns. The most common active site on cation exchange resins is the sulphonic acid group $-SO_3^-H^+$, a strong acid. For an anion exchanger, a common active exchange group is the tertiary amine group $-N(CH_3)_3^+OH^-$, a strong base.

The exchange process of a solution, which contains a cation M^{x+} on a cation exchange column, can be described by the equilibrium

$$xRSO_3^-H^+\,(\text{solid}) + M^{x+}\,(\text{solution}) \rightarrow (RSO_3^-)_xM^{x+}\,(\text{solid}) + xH^+\,(\text{solution})$$

where $RSO_3^-H^+$ represents one of the many exchange groups attached to a large polymer molecule.

Similarly, a strong base exchanger interacts with the anion, A^{x-}, as shown by the reaction

$$\mathrm{xRN(CH_3)_3OH^-\,(solid) + A^{X-}\,(solution) \rightarrow [RN(CH_3)_3^+]_x A^{X-}\,(solid)}$$
$$\mathrm{+\ xOH^-\,(solution)}$$

For an example of the application of the mass-action law to ion exchange equilibria, the reaction between a singly charged ion B^+ with a sulphonic acid resin held in a column can be considered. From a neutral solution, initial retention of B^+ ions at the head of the column occurs because of the equation

$$\mathrm{RSO_3^-H^+\,(s) + B^+\,(aq) \rightleftharpoons RSO_3^-B^+\,(s) + H^+\,(aq)} \qquad \text{...2.8}$$

Elution with a dilute solution of hydrochloric acid shifts the equilibrium to the left, causing part of the B^+ ions in the stationary phase to be transferred to the mobile phase. These ions move down the column in a series of transfers between the stationary and the mobile phases.

The equilibrium constant (K_{ex}) for the exchange reaction in equation 2.8 takes the form

$$K_{ex} = \frac{[\mathrm{RSO_3^-B^+}]_s[\mathrm{H^+}]_{aq}}{[\mathrm{RSO_3^-H^+}]_s[\mathrm{B^+}]_{aq}} \qquad \text{...2.9}$$

Rearranging gives

$$\frac{[\mathrm{RSO_3^-B^+}]_s}{[\mathrm{B^+}]_{aq}} = K_{ex}\frac{[\mathrm{RSO_3^-H^+}]_s}{[\mathrm{H^+}]_{aq}} \qquad \text{...2.10}$$

During the elution, the aqueous concentrations of hydronium ions are much larger than the concentrations of singly charged B^+ ions in the mobile phase. Furthermore, the exchanger has an enormous number of exchange sites relative to the number of

B^+ ions being retained. Thus, the overall concentrations of $[H^+]_{aq}$ and $[RSO_3^-H^+]_{(s)}$ are not significantly affected by shifts in the equilibrium 2.8. Therefore, when $[RSO_3^-H^+]_{(s)} >> [RSO_3^-B^+]_{(s)}$ and $[H^+]_{(aq)} >> [B^+]_{(aq)}$, the right side of equation 2.10, is substantially constant, and it can be written as

$$\frac{[RSO_3^- B^+]_s}{[B^+]_{aq}} = K = \frac{c_s}{c_m} \qquad ...2.11$$

where K is the distribution constant.

K_{ex} in equation 2.10 represents the affinity of the resin for the ion B^+ relative to other ions (here, H^+). Where K_{ex} is large, a definite tendency exists for the solid to retain B^+ ; where K_{ex} is small, the reverse is observed. For a typical sulphonated cation exchange resin, values for K_{ex} decrease in the order (Skoog et. al,1998)

$Tl^+ > Ag^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+$.

For divalent cations, the order is

$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+}$.

For a strong base resin, the order for anions is

$SO_4^{2-} > C_2O_4^{2-} > I^- > NO_3^- > Br^- > Cl^- > HCO_2^- > OH^- > F^-$.

These conditions depend on various factors, such as the type of resin, size of the hydrated ion, and so on.

2.2.2.2 Ion Exchange Packings

Historically, ion-exchange has been performed on small, porous beads formed during emulsion copolymerization of styrene and divinyl benzene (Skoog et. al., 1998). Divinyl benzene provides cross-linking, which imparts mechanical stability to the beads. In order to make the polymer active towards ions, acidic or basic functional groups are chemically bonded to the structure. The common active sites for cation-exchange resin are the sulphonic acid group. Anionic exchangers commonly contain tertiary amine groups.

Porous polymeric packings, as applied in High Performance Liquid Chromatography (HPLC), have disadvantages such as the slow rate of diffusion of analyte molecules through the micropores of the polymer matrix and the compressibility of the matrix. To overcome these shortcomings, newer columns such as the pellicular bead packing and coated porous silica microparticles packing were developed. In pellicular packing, the surface of a relatively large (30-40 micrometers), nonporous, spherical, glass or polymer bead is coated with a synthetic ion exchange resin. The silica packing is prepared by coating porous microparticles of silica with a thin film of exchanger. In these packings, faster diffusion in the polymer film leads to enhanced efficiency (Skoog et. al., 1998).

However, in ion chromatography, the stationary phase is a polystyrene/divinyl benzene based resin because this is much more stable to pH than silica based support material (Joachim, 1986). Whereas silica can be used between pH 3 and 9, ion chromatography separators are stable between pH 0 and 14. The pH stability allows the use of extreme pH values that can convert molecular compounds such as sugars and alcohols into ionic species.

2.2.2.3 Ion Exchange Chromatography with Eluent Suppressor Columns

Conductivity detectors are commonly used in ion chromatography mainly because they are highly sensitive, universal for charged species and predictably responsive to concentration changes. However, the high electrolyte concentration required to elute most analyte ions within a reasonable period tends to produce high conductivities that swamp the conductivity from analyte ions, thus reducing the detector sensitivity.

The problem of high eluent conductance is solved by the introduction of an eluent suppressor column immediately following the analytical column. The suppressor column is packed with an ion-exchange resin that effectively converts the solvent ions to a molecular species of limited ionization without affecting analyte ions. For example, when cations are determined, HCl if often used as eluent. The suppressor column is an anion exchanger in the hydroxide form. The product of the reaction in the suppressor is water:

$H^+(aq) + Cl^-(aq) + Resin^+OH^-(s) \rightleftharpoons Resin^+Cl^-(s) + H_2O(l)$.

In anion separation, the suppressor packing is the acid form of a cation exchange resin. In this case, sodium bicarbonate or carbonate, or even a mixture of the two, serve as eluent. For sodium bicarbonate eluent, the reaction in the suppressor may be represented as

$Na^+(aq) + HCO_3^-(aq) + Resin^-H^+(s) \rightleftharpoons Resin^-Na^+(s) + H_2CO_3(aq)$.

The largely undissociated carbonic acid does not contribute significantly to the background conductivity.

In recently designed commercial instruments, the regeneration of the suppressor columns is effected automatically with electrogenerated hydrogen or hydroxyl ions so that interruptions in the use of the instruments for regeneration are not required (Skoog et. al., 1998).

2.2.2.4 Instrumental requirements for Ion Chromatography

An ion chromatograph has four basic instrumental requirements, namely a reagent delivery mode, a separation mode, a detection mode and a data collection mode. The four instrumental requirements, as applicable to the Dionex 4000i Chromatograph as it was used in this study, are discussed below.

▸ Delivery mode

This part of the Ion Chromatograph consists of an eluent reservoir, the pump and the sample injector. The eluent reservoirs are usually made of glass, although sometimes plastic material may be used, depending on the type of eluent to be handled. The pump used in this study was a constant pressure/constant flow type. A loop valve injector was used.

▸ Separation mode

The analytical column used for this study is the Dionex AS14 column. The AS14 column is made of a stationary phase derived from a polystyrene based resin which has been cross-linked (2 %) with divinyl benzene. For the analysis of anions, the hydrophobic core resin has been functionalized with totally permeable latex particles that are completely aminated. The nature of the column material enables it to handle solutions within the pH range 0 – 14.

- **Detection mode**

This mode consists of the suppressor device (for suppressed conductivity) and the actual detection device. A good detector should have a high sensitivity, low noise, a wide linear range, and it should respond to all types of ions. No highly sensitive universal detector is, however, available for liquid chromatography. The nature of the sample plays a prominent role in the choice of a suitable detector. Commonly used detectors for ion chromatography are: conductivity, UV-Vis, electrochemical and fluorescence detectors. The detector type used in this study is the Dionex conductivity detector.

A conductivity detector possesses most of the desirable properties, such as linear response, stability, low noise and high sensitivity. Conductivity detectors are universal for charged species. They respond in a predictable way to changes in concentration. Furthermore, such detectors are easy to miniaturize, and ordinarily give a long, trouble-free service.

Suppressed conductivity requires the use of ion exchange techniques to chemically lower the background conductivity of the eluent prior to detection by conductivity. The suppressor also converts the solute ions to their corresponding acids or hydroxides, which have high conductivities. This results in increased detection sensitivity for the respective solute ions. The lowering of background conductivity also results in increased detector sensitivity.

- **Data collection mode**

The results of a chromatographic separation are processed through a data collection device. Such a device could be a printer, integrator or more commonly a computer. Various computer software packages are commercially available. Chromperfect software was used in this study.

2.2.2.5 Advantages of Ion Chromatography

Ion chromatography offers several advantages over conventional wet chemical methods such as photometry, gravimetry, turbidimetry and colorimetry. The relative advantages include, among others, speed, sensitivity, selectivity and simultaneous analysis.

- **Speed**

A baseline resolved separation of a mixture of ions can be achieved within a short period. For example, a chromatogram of a seven component inorganic anionic mixture is easily obtainable within six minutes. The high speed with which quantitative analysis can be conducted vastly increases the sample throughput as compared to the time consuming traditional wet methods.

- **Sensitivity**

The introduction of the microprocessor technology has made it possible to identify ions in the middle to lower ppb range without the need for preconcentration. Detection limits in the picomole range can be achieved for amino acid analysis (Joachim, 1986). The direct injection techniques have a detection limit for simple anions of approximately 10 ppb (Weiss, 1986). Sample enrichment on a concentrator column permits the analysis of even carefully deionized water for the presence of chloride, sulphate and/or sodium ions. Using this preconcentration method, the detection limit for simple anions can be reduced to approximately 0.010ppb. Tarter (1987) lists a detection limit of 5 ppb for fluoride ion analysis in a 50μL sample solution by eluent suppressed ion chromatography. Lower detection limit values can be obtained by appropriate concentration techniques and/or large injection volumes.

- **Selectivity**

Careful choice of a suitable separation and appropriate detection system ensures selectivity of ion chromatography. Heavy and transition metals, polyvalent anions, and silicate can be determined with improved selectivity with the aid of post-column derivatization.

- **Simultaneous Analysis**

In ion chromatography, one can obtain an anion or cation profile that provides information on the composition of a sample in a single run. This advantage rivals conventional wet analytical methods as well as other instrumental techniques, such as potentiometry and AAS.

2.2.3 Willard and Winter standard method of fluoride analysis

During the 1960s fluoride was separated by the Willard and Winter steam-distillation method and then determined by a titration procedure (Willard and Winter, 1933). The Willard and Winter method is the standard method of determination of fluoride in inorganic materials (Scott, 1979; Peters and Ladd, 1971). A standard method is one which has been proved to be reliable and against which new methods are compared. The reagents for the Willard and Winter method are Zirconium nitrate (1 gram $Zr(NO_3)_4 \cdot 5H_2O$ in 250 mL water) and Alizarin red (1 gram of sodium alizarin sulphonate in 100 mL ethanol). The undissolved residue of the alizarin red solution is filtered off and 150 mL ethanol is added to the filtrate. The two solutions, zirconium nitrate and alizarin red, are kept in stock and mixed, in the proportion of 3 parts zirconium nitrate solution to 2 parts alizarin red solution, as needed.

Procedure 1:

The sample is prepared in accordance with the fusion procedure, described by Peters and Ladd (1971), given in Section 2.1.1. The pH of a measured aliquot of the fluoride sample is adjusted to between 3.00 and 3.05. After the addition of the sodium alizarine sulphonate solution, the solution is titrated to a pink colour with a standard thorium solution. In order to avoid the possibility of explosions in the fusion stage, sulphuric acid may be used instead of the perchloric acid-phosphoric acid mixture.

Procedure 2:

The pulverized gypsum (0.1 to 0.5g), accurately weighed to a mg unit, is steam distilled in the presence of finely powdered silica and sulphuric acid (Murakami, 1968). The vaporized silicon fluoride is collected into a sodium hydroxide solution where sodium silicofluoride is formed. The total fluoride amount is then determined colorimetrically by the Th-alizarine method.

2.2.4 Pyrohydrolysis method of fluoride analysis

Fluoride has been determined using a pyrohydrolysis technique in which a sample, such as rock or other refractory material, is heated at very high temperatures of 1000 °C with super heated steam. The HF thus formed is collected and the amount of fluoride determined (Clement and Seargent, 1971).

2.3 Aim of Study

The aim of this study is to compare three analytical methods, namely, Willard and Winter standard method of fluoride analysis, the Ion-Selective Electrode method, and Ion Chromatography as applied in the quantification of fluoride in chemical gypsum. Secondly, the efficiency of treatment of the chemical gypsum with a developed water, lime and sulphuric acid treatment is investigated.

The research strategy was organized to glean as much information as possible about South African chemical gypsum by using Kynoch phosphogypsum as the main target sample and the Omnia phosphogypsum and Tioxide titangypsum as supporting samples. To this end, the particle size distribution and studies regarding the extent of fluoride impurities in different pretreated samples were focussed on the Omnia phosphogypsum and compared to the Kynoch phosphogypsum. The Tioxide titangypsum, which was brought on later in the research, was found to contain the lowest fluoride levels compared to Kynoch and Omnia phosphogypsums. Hence, Tioxide titangypsum and Kynoch phosphogypsum were used mainly to investigate how the results obtained through different analyses procedures, namely, Ion Selective Electrode method, Ion Chromatography method and the Willard and Winter method, compared to one another. The fluoride levels in Tioxide titangypsum were also compared to those in the Kynoch phosphogypsum.

The standard method of fluoride analysis, the Willard and Winter method, is based upon distillation of fluoride from the sample. The accuracy of methods involving distillation is suspect, particularly for materials with a high alumina content. This is because fluorine, being the most electronegative element, forms strong bonds with other elements (Javellana and Jawed, 1981). In addition, fluoride forms strong complexes with iron, chromium, silicon and other polyvalent ions. The Willard and Winter method is also known to be very slow and tedious (Peters and Ladd, 1971). There is thus a need to research other analytical methods that may be faster and more accurate in the determination of fluoride.

The Ion-selective electrode method is fast and the equipment is inexpensive. The main advantage of ion chromatography is that with a single run, the chromatogram depicting all ions in the sample can be obtained. The procedure is slower than the Ion-selective electrode method but the sample throughput can be improved with the use of higher flow rates and the utilization of microbore columns.

CHAPTER 3 Composition of South African Chemical Gypsum

3.1 Introduction

The samples of chemical gypsum that were investigated in this study were sourced from two phosphate fertilizer manufacturing plants, and from a titanium dioxide pigment producing plant. The two phosphate fertilizer plants in question are Kynoch and Omnia, both situated in the Northwest Province. The titanium dioxide plant is Tioxide, situated in KwaZulu-Natal. The two phosphate fertilizer manufacturers produce phosphogypsum as a by-product during the phosphoric acid production process while Tioxide produces titangypsum as a co-product of the titanium dioxide manufacturing process.

3.2 Kynoch phosphogypsum

The Kynoch phosphate fertilizer plant utilizes the wet process in the manufacture of phosphoric acid. The phosphate rock is transported from Phalaborwa in the Limpopo Province to the Kynoch plant, which is situated in Potchefstroom in the Northwest Province.

The phosphate rock is initially crushed into very fine particles. It then undergoes a sulphuric acid attack with an acid of a concentration of between 72 % and 98 % (m/m). The reaction products are phosphoric acid and phosphogypsum. The phosphogypsum is filtered in filtration pans to recover the produced phosphoric acid. The concentration of phosphoric acid that is produced, expressed as percent

P_2O_5, is approximately 12 %. Multiple water washing stages are performed on the phosphogypsum residue to recover as much phosphoric acid as possible. During the washing of the residue phosphogypsum with water in the first stage, the resulting phosphoric acid concentration is approximately 9 % P_2O_5, and the last washing step results in a phosphoric acid concentration of approximately 5 % P_2O_5. The phosphoric acid is concentrated to a final concentration of approximately 50 % P_2O_5.

The phosphogypsum that is produced at this plant amounts to several hundreds of thousands of tonnes per annum. A fraction of this phosphogypsum is sold to the cement industry. An even smaller portion is sold to the agricultural industry. The bulk of this phosphogypsum is disposed of on land and stored as phosphoypsum stacks which are situated about three kilometres away from the plant.

3.3 Omnia phosphogypsum

The process of phosphoric acid production at the Omnia phosphate fertilizer plant is similar to that discussed above at the Kynoch fertilizer plant. However, Omnia phosphogypsum was chosen as one of the samples in this study since the concentrations of impurities in phosphogypsum may differ from plant to plant, depending on the type of phosphate rock used in chemical processing and on the temperature, redox conditions and chemical composition within the sulphuric acid digester.

3.4 Tioxide - Titangypsum

The Tioxide pigment plant is situated in Durban in the Kwazulu-Natal province of

South Africa. It is part of the Huntsman Tioxide group whose core business is the production of TiO_2. The titangypsum in this particular plant is a co-product because it is produced, not as a by-product, but separately from the main production process of the titanium dioxide.

Titanium dioxide is the white pigment most commonly used world wide to lend whiteness, opacity and protection to manufactured products. It is used in a variety of industrial and household products, including paints, plastics, paper, printing inks, ceramics, food, cosmetics and textiles.

At Tioxide, titanium dioxide is produced from the raw material obtained from the surrounding area which is rich in titanium. The ilmenite ore is treated with concentrated sulphuric acid (98 %) and accordingly controlled in order to produce the pigment. At the end of the process, an effluent stream which is rich in sulphate (about 15 to 20 percent sulphuric acid) is channelled to the gypsum plant. At this stage, the effluent is treated with limestone found in the local area, and appropriately controlled to produce the chemical gypsum.

The waste stream from the pigment plant contains a high concentration of iron (about 3 % Fe), which is precipitated by passing it through high purity oxygen. The precipitated ferric oxide causes the chemical gypsum thus produced to change colour from its normal white to a reddish-brown. Hence this gypsum is normally referred to as red gypsum.

A portion of the titangypsum is currently used in the agricultural field as a soil conditioner for acidic soils. A small percentage is sold to the cement industry for use as setting time retarder. The rest is disposed of on land.

3.5 XRF analysis of South African chemical gypsum

The samples of South African chemical gypsum, namely Kynoch phosphogypsum, Omnia phosphogypsum and Tioxide titangypsum, were analysed in order to determine the chemical composition of each.

Samples:

Kynoch Phosphogypsum, Omnia phosphogypsum and Tioxide chemical gypsum (TCGU)

Analysis:

The sample was dried at 110°C, cooled in a desiccator and ground to <75µm in a Tungsten Carbide milling vessel. It was then roasted at 1000°C to determine Loss On Ignition value. Then 1.000g of the sample was mixed with 6.000g $Li_2B_4O_7$ in a platinum crucible and fused into a glass bead. Major element analyses were executed on the fused bead using the ARL9400XP+ spectrometer.

Results:

The results are given in Table 3.1. LOI represents loss on ignition.

Table 3.1: Major species analysis of South African Titangypsum(TCGU), Kynoch and Omnia phosphogypsums.

%	**TCGU**	**Kynoch**	**Omnia***
$\mathbf{SiO_2}$	3.10	<0.01	n/d
$\mathbf{TiO_2}$	0.65	0.02	-
$\mathbf{Al_2O_3}$	0.64	0.08	0.04
$\mathbf{Fe_2O_3}$	4.49	<0.01	0.05
MnO	0.07	<0.01	n/d
MgO	0.48	0.04	0.16
CaO	36.48	38.24	38.38
$\mathbf{Na_2O}$	<0.03	<0.03	n/d
$\mathbf{K_2O}$	0.03	<0.01	n/d
$\mathbf{P_2O_5}$	0.05	1.93	1.68
$\mathbf{Cr_2O_3}$	0.09	<0.01	n/d
NiO	<0.01	<0.01	-
$\mathbf{V_2O_5}$	0.17	<0.01	n/d
$\mathbf{ZrO_2}$	0.09	<0.01	n/d
$\mathbf{SO_3}$	48.70	54.10	51.24
LOI	4.36	4.41	10.06
TOTAL	99.44	98.93	101.47

*Omnia obtained from Van Der Merwe (2001). n/d means not detected

3.6 Discussion and conclusion

The results of the analyses of the chemical gypsum samples given in (Table 3.1) showed that titangypsum was different in composition when compared to the Kynoch and Omnia phosphogypsums. Titangypsum contained about 0.6 % titanium dioxide while the Kynoch phosphogypsum contained much lower amounts of trace levels. Notably, it was found that titangypsum contained about 4 % Fe_2O_3 while the Kynoch phosphogypsum contained very low levels of less than 0.01 % Fe_2O_3 and

Omnia contained 0.05 %Fe_2O_3. The amount of SiO_2 in titangypsum was about 3 % while Kynoch phosphogypsum contained trace levels only and it was not detected in Omnia phosphogypsum. The CaO content of titangypsum was 36.5 % while Kynoch phosphogypsum contained 38.2 % CaO and Omnia phosphogypsum contained 38.4 %CaO. The Kynoch and Omnia phosphogypsums contained 54.1 % SO_3 and 51.2 % SO_3 respectively compared to 48.7 % SO_3 present in titangypsum. The composition of pure gypsum, $CaSO_4{\cdot}2H_2O$, is determined by calculation to be 32.6 % CaO, 46.5 % SO_3 and 20.9 % water. Hence, Titangypsum contained slightly more SO_3 than pure gypsum, while Kynoch and Omnia phosphogypsums contained a significantly higher amount of SO_3 compared to pure gypsum. The CaO content of pure gypsum is less than that contained in all samples of titangypsum, Kynoch and Omnia phosphogypsum analysed. The difference in composition of these chemical gypsums emanates chiefly from the type of production process but more importantly from the nature of the raw material.

The presence of aluminium, silicon and iron in the chemical gypsum sample matrix is a cause for concern because these species are potential sources of interferences. The sample preparation method needs to take into account this potential threat if the results are to be credible. The choice of the sample sintering method using ZnO-Na_2CO_3 mixture as discussed in Sections 5.1 and 5.2 was based on these considerations.

CHAPTER 4 Removal of Fluoride Impurities from South African Chemical Gypsum

4.1 Introduction

Various methods have been applied by different researchers to remove fluoride impurities from phosphogypsum (Chapter 1, Section 1.3). The methods of treatment of South African chemical gypsum investigated in this work are the sieving of samples, washing the samples with water, milk of lime, and diluted sulphuric acid. The samples studied were generally dried at 45 °C overnight. This was in line with the standard methods for chemical analysis of gypsum and its product (ASTM C-471-76), which state that the free water content can be determined without removing the chemically combined water by drying at 45 °C (Gadalla et al,. 1987). The procedure followed in each of these purification techniques is briefly outlined in the following sections. The extent of fluoride removal by each of these methods is reported in Chapter 7 and 8.

4.2 Physical treatment – Sieving

Phosphogypsum has been purified by using a physical method, as published by Al-Jabbari et al., prior to using it as a building material (cited by Smadi et al., 1999). These authors washed the phosphogypsum with water using sieve no.100, and heated it at various temperatures. Calcium hydroxide was then added as an accelerator to improve the setting time and the compressive strength of the produced material.

In this work the particle size distribution of dried Omnia and Kynoch phosphogypsums was determined.

4.2.1 Sample size distribution measurements

Two samples of phosphogypsum, Omnia and Kynoch, were obtained from two South African phosphate fertilizer producers. The samples were dried overnight at 45°C. A 10.0g mass of each sample was sieved for ten minutes on a Fritsch Analysette 3 vibrator sieve shaker with a set of sieves ranging in size from 75 µm to 1700 µm.

4.2.2 Results and discussion

The particle size distribution results for Omnia and Kynoch phosphogypsum samples are given in Table 4.1.

Table 4.1: Particle size distribution for Kynoch and phosphogypsum

Sieve size (µm)	Omnia phosphogypsum (%)	Kynoch phosphogypsum (%)
75	37.1	47.5
150	48.7	27.7
300	14.1	11.1
600	0.1	3.6
1700	0	5.4
>1700	0	4.6

The results showed that, compared to the Kynoch sample, the Omnia phosphogypsum possessed finer particles. About 10% of Kynoch particles have a particle size larger than 600 μm, whereas all Omnia phosphogypsum particles are smaller than 600 μm.

4.3 Chemical gypsum treatment with water and milk of lime

Smadi et al.(1999) purified the phosphogypsum by washing the sample with water, followed by calcining at various temperatures (170°C to 950°C). They observed that the total amount of fluoride in unwashed phosphogypsum decreased progressively from 2.12% (170°C) to 0.16%° (950°C). The total amount of fluoride in the washed sample decreased progressively from 0.89% (170°C) to 0.27% (950°C).

Ölmez and Erdem (1989) also managed to remove water soluble impurities such as fluorosilicic acid from phosphogypsum samples by treatment with water and milk of lime. Research has also shown that impurities such as phosphates and fluoride can be minimized by treatment of the phosphogypsum with lime water or aqueous cement extracts (Tabikh and Miller, 1971). This converts acid phosphates into $Ca_3(PO_4)_2$ and complex fluoroanions into CaF_2 .

In this study, a water wash and milk of lime treatment were conducted on the chemical gypsum samples, followed by a thermal treatment at 900°C. This procedure is a combination of the pretreatment methods of Smadi et al. and other researchers such as Ölmez and Erdem and Tabikh and Miller, as discussed above.

For lime washed samples, a 0.1 % (m/m) milk of lime solution was prepared by weighing 0.1g calcium hydroxide into a beaker and adding deionised water to give a 100g solution. The mixture was thoroughly mixed and then the undissolved calcium hydroxide left to settle. The supernatant liquid was used to wash the chemical gypsum samples. A 12%(m/v) slurry of phosphogypsum (Omnia or Kynoch) was prepared in the 0.1%(m/m) milk of lime solution. The mixture was filtered with a Whatman 41 filter paper and then dried in an oven at 45 °C overnight. The water washed samples were treated in a similar way to the lime washed samples.

4.4 Diluted sulphuric acid treatment

Jarosiński (1994) described a method in which the phosphogypsum sample is first leached in a 12% (mass percentage) sulphuric acid solution to recover rare earth elements, and then converted into anhydrite II (different phases of gypsum, including anhydrite II are described in detail in Chapter 11) in a 50% sulphuric acid solution. This method was found to be successful in removing some of the undesirable impurities, such as phosphorous, fluorine and sodium. The amount of fluoride was reduced from a total of 0.39 % (m/m) to 0.04% after leaching with the 12% sulphuric acid, and was eventually reduced to 0.00% in the anhydrite. Jarosiński suggests a reduction of the levels of phosphate and fluorine to about 0.8% and 0.2% respectively before the phosphogypsum can be used as a substitute for natural gypsum as a set retarder in cement.

In this study, the method followed by Jarosiński was adapted for the treatment of Kynoch and Omnia phosphogypsum samples. Titangypsum samples were sourced later in the project and it was found that the untreated samples already contained an insignificantly low fluoride amount, hence it was not deemed necessary to subject them to the sulphuric acid treatment. A heater stirrer was used to perform the leaching. Using a solid/liquid mass ratio of 1:2 for the Omnia phosphogypsum, a thick paste was formed. This could not be effectively stirred by the magnetic stirrer. This then resulted in the use of a solid/liquid ratio of 1:4 for the Omnia phosphogypsum and 1:2 for the Kynoch phosphogypsum. The same method was used in a PhD thesis (Van der Merwe,2001). The experimental conditions followed in this study are summarised in Table 4.2.

Table 4.2: Adapted experimental conditions used to purify and recrystallize Omnia and Kynoch phosphogypsum

	Leaching	
Parameters	**Kynoch**	**Omnia**
Temperature	40°C	40°C
Sulphuric acid concentration (mass %)	12%	12%
Solid/liquid mass ratio	1 : 2	1 : 4
Time of stirring	45 min	45 min
Sample mass	15.0 g	15.0 g

Chapter 5 Sample preparation

5.1 Introduction

In many reactions of fluorine with metal ions, sparingly soluble compounds which are not easy to dissolve are often formed. Hence, in analytical procedures, interference from other ions present in the sample is considerable. This may occur either by the formation of sparingly soluble fluorides or by the combination with other metal ions to form strong metal-fluoride complexes (Williams, 1979).

Silicate materials are usually prepared by fusion with $LiBO_2$ followed by acid dissolution. However, all the Si, Al and Fe of the sample are retained in the solution. These cations interfere in the determination of fluoride by the ion-selective electrode method and ion chromatography (conductivity detection) since fluoride has to be determined as F^-. In this study, the sample is sintered with a mixture of ZnO-Na_2CO_3 in order to reduce the interference of these cations. The silicates and aluminates are left behind as insoluble zinc silicates and aluminates (Scott, 1979; Javellana and Jawed, 1981).

Chemical gypsum samples are complex and heterogeneous in composition. This emanates mostly from the composition of the raw material and the production processes. In this study, each gross sample was therefore given a specific batch number to keep track of the bulk samples that were produced under the same reaction conditions.

5.2 Experimental

5.2.1 Chemicals

Na_2CO_3:	Analysed Analytical reagent (AAR), Anhydrous, SMM Chemicals (Pty) Ltd
ZnO:	Merck (garantiert reine Reagenzien)

5.2.2 Procedure for sample preparation

A chemical gypsum sample is dried overnight at 45 °C, as recommended in ASTM C-471-76 cited by Gadalla et al. (1987). The sample is cooled in a desiccator and ground with piston and mortar to fine particles and then mixed thoroughly. This represents the unwashed sample. For a water washed sample, a slurry of the unwashed sample is prepared in water to produce a mixture of 12% (by mass). The mixture is stirred on a magnetic stirrer for 10 minutes and then filtered. The residue is dried overnight at 45 °C. It is then cooled in a desiccator, ground with piston and mortar to fine particles and mixed thoroughly. This represents the water washed sample. The lime washed sample is prepared from the unwashed sample according to a similar method used for the water washed sample, using a 0.1% (m/m) milk of lime solution instead of water. The 0.1 % (m/m) milk of lime solution was prepared by weighing 0.1g calcium hydroxide into a beaker and adding deionised water to give a 100g solution. The mixture was thoroughly mixed and then the undissolved calcium hydroxide left to settle. The supernatant liquid was used to wash the chemical gypsum samples. The acid treated sample is prepared as explained in the modified Jarosiński procedure in Section 4.4. The unwashed chemical gypsum sample is prepared as a slurry using 12% (m/m) diluted sulphuric acid. A solid/liquid ratio of 1:4 for the Omnia phosphogypsum and 1:2 for the Kynoch phosphogypsum is maintained. A heater stirrer is used to perform the leaching at 40°C for a period of 45 minutes. The sample is filtered with a Whatman 41 filter paper and the residue dried overnight at 45°C. It is then cooled in a desiccator, ground with piston and mortar to fine particles and mixed thoroughly. This represents the acid treated sample.

5.2.3 Sample fusion procedure

The chemical gypsum is accurately weighed to 0.1mg in an ignited platinum crucible. A flux of sodium carbonate (dehydrated)- zinc oxide is added such that the mass ratio of chemical gypsum : sodium carbonate : zinc oxide is 1:4:0.8. The crucible is left for 30 minutes in an oven at 900°C. After the crucible has cooled down, it is placed in a 100 mL plastic beaker. The contents are dissolved in approximately 80 mL water. Once the platinum crucible has been removed from the beaker, a few drops of concentrated nitric acid are added until the solution becomes clear and no more CO_2 is evolved. During this process, the pH of the solution is monitored with a pH meter. The final pH is kept at slightly above 5. The solution is filtered off with a Whatman 41 filter paper and transferred to a volumetric flask. The flask is filled to the mark with deionised water.

Dissolution occurs at a very slow rate and may take several hours. The sample may be left undisturbed overnight to aid the dissolution process. It is helpful to place a stirring rod in the crucible with its hardened contents. This allows the entire crucible to rotate in the beaker. Warming the crucible up again to 80°C is also helpful in releasing the contents. The acid should be added very slowly to avoid the CO_2 being released too violently, causing the crucible contents to spill over.

5.2.4 Ion selective electrode method – samples

The ion-selective electrode for fluoride determination is made from a LaF_3 membrane. This membrane is selective to fluoride ions and will be unable to detect them if they are bound or complexed. The electrode response is also pH dependent. In order to optimize the availability of fluoride in its ionic form, the pH is buffered just above pH 5. This is to avoid the formation of HF and HF_2^- at pH values below 5. In alkaline solutions the electrode is sluggish and higher fluoride concentrations are indicated. A total ionic strength buffer (TISAB) is therefore mixed with the samples (50:50) to maintain the solution pH and also to maintain a constant ionic strength. The TISAB solutions are usually mixed with chelating agents such as sodium citrate to complex Al, Si and Fe. Various authors have made intensive studies regarding the efficacy of ionic strength buffers (Raghavan et. al, 1992). The two buffer solutions mentioned below were tested against each other and found to be equaly effective for fluoride determination in samples as complex as chemical gypsum (Section 10.2).

The preparation procedure of each of the two buffer solutions used in this study are described below.

Buffer 1: 58.00g sodium chloride is dissolved in deionised water and transferred into a 500mL beaker. 0.30g sodium citrate is dissolved in deionised water and mixed with the sodium chloride solution. 57mL of glacial acetic acid is added to the mixture and the pH adjusted to 5.0 with 6M NaOH. The buffer solution is then transferred to a 1L volumetric flask and brought up to the mark with deionised water.

Buffer 2: 20.0g citric acid is dissolved in deionised water and transferred to a 500mL beaker. 68.0g sodium nitrate is dissolved in deionised water and mixed with the citric acid solution. 28.0g NaOH is dissolved in 100mL water and added to the mixture. 57mL of glacial acetic acid is added to the mixture and the pH adjusted to 5.5 with 6M HCl. The buffer solution is then transferred to a 1L volumetric flask and brought up to the mark with deionised water.

5.2.5 Ion Chromatography – samples

The samples are prepared using the fusion technique described in Section 5.2.3. Each sample is then filtered and injected into the chromatograph.

Chapter 6 Data Handling

6.1 Introduction

Because of experimental errors, any measurement, no matter how carefully performed, contains some degree of uncertainty. This chapter is concerned with the definition of terms used to express uncertainty and derivation of the relevant statistical equations that have been used in this study. The chapter also covers statistical equations that have been used to discard or retain any suspicious experimentally obtained measurement.

6.2 Definition of terms

The terms used in this study to describe the experimentally obtained measurements are (1) mean, (2) sample standard deviation, (3) relative standard deviation, (4) pooled standard deviation, and (5) Q-test. Each of these terms is described below.

6.2.1 Mean

The mean, $\overline{x}$, is the quantity obtained by dividing the sum of replicate measurements by the number of measurements in a set (Skoog et al., 1997). The equation is

$$\text{Mean } (\overline{x}) = \frac{\sum_{i=1}^{N} x_i}{N} \qquad \ldots 6.1$$

where x_i is the *i*th measurement and N is the number of measurements.

6.2.2 Sample standard deviation

The sample standard deviation (*s*) is an indication of the precision of the measurement (Skoog et al., 1997). It is a quantitative measure of the reproducibility of results. For a finite number of measurements, the standard deviation is determined by the equation:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N - 1}} \qquad \text{...6.2}$$

The term N-1 in the denominator is the degree of freedom.

6.2.3 Relative standard deviation

The relative standard deviation (RSD) is obtained by dividing the standard deviation by the mean of the set of data. It is expressed as a percentage when the ratio is multiplied by 100%. The equation is given as:

$$\mathrm{RSD} = \frac{s \times 100\%}{\bar{x}} \qquad \text{...6.3}$$

At times it is expressed in parts per thousand (ppt) when the ratio between the standard deviation and the mean is multiplied by 1000 ppt.

6.2.4 Pooled standard deviation

The data for a series of similar samples analysed in the same way can be pooled to provide an estimate of the standard deviation that is superior to the value of the standard deviation obtained for any individual subset (Skoog et al., 1997). To obtain an estimate of the pooled standard deviation, s_{pooled}, deviations from the mean for each subset are squared; the squares of all subsets are then summed and divided by an appropriate number of degrees of freedom. The equation used for computing s_{pooled} for *t* sets of data may be expressed as:

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1}(x_i - \bar{x}_1)^2 + \sum_{j=1}^{N_2}(x_j - \bar{x}_2)^2 + \sum_{k=1}^{N_3}(x_k - \bar{x}_3)^2 + \ldots}{N_1 + N_2 + N_3 + \ldots - N_t}} \qquad \ldots 6.4$$

where N_1 is the number of data in set 1, N_2 is the number of data in set 2, and so forth. N_t is the total number of data sets that are pooled.

6.2.5 Q-test

Sometimes a result obtained experimentally appears to deviate greatly from other values. If nothing points to the possibility of determinate error in the process used to obtain the result, it should not be discarded unless so indicated by some statistical test. Q-test is one such statistical method for checking whether an outlier should be retained or discarded. In this test the absolute value of the difference between the questionable result, x_q, and its neighbour, x_n, is divided by the range of the entire set, w, to give the quantity Q_{exp}. The equation used to calculate Q_{exp} is:

$$Q_{exp} = \frac{|x_q - x_n|}{w} \qquad \ldots 6.5$$

where w is the difference between the highest value in a set and the lowest.

The ratio is then compared with rejection values Q_{crit} found in most statistical tables (e.g. Table 2.3 in Christian, 1994). If Q_{exp} is greater than Q_{crit} then the questionable result can be rejected with the indicated degree of confidence.

6.3 Least squares method

The object of this method is to find the straight line for which the sum of the squares of the distances between the data points and the line is a minimum. In the derivation of the equation for the best straight line, it is assumed that there is a linear relationship between the dependent variable (*y*) and the independent variable (*x*). In most analytical methods, the measured quantity *y* is plotted as a function of the known concentration *x* of a series of standards. The equation for the straight line is given as:

$$y = mx + b \qquad \ldots 6.6$$

where *b* is the *y* intercept and *m* is the slope of the line. The following quantities are defined for experimental data prior to any empirical derivation of the least squares equation (Skoog et al., 1997):

$$S_{xx} = \sum (x_i - \bar{x})^2 = \sum x_i^2 - \frac{(\sum x_i)^2}{N} \qquad \ldots 6.7$$

$$S_{yy} = \sum (y_i - \bar{y})^2 = \sum y_i^2 - \frac{(\sum y_i)^2}{N} \qquad ...6.8$$

$$S_{xy} = \sum (x_i - \bar{x})(y_i - \bar{y}) = \sum x_i y_i - \frac{\sum x_i \sum y_i}{N} \qquad ...6.9$$

where x_i and y_i are individual pairs of data for x and y, N is the number of pairs of data used in preparing the calibration curve, and $\bar{x}$ and $\bar{y}$ are the means for the variables.

The slope (*m*)of the line is determined by the equation

$$m = \frac{S_{xy}}{S_{xx}} \qquad ...6.10$$

The intercept (*b*) is determined by the equation

$$b = \bar{y} - m\bar{x} \qquad ...6.11$$

To compute the standard deviations of the slope and intercept, the standard deviation about the regression, s_r, must first be computed from the equation

$$s_r = \sqrt{\frac{S_{yy} - m^2 S_{xx}}{N - 2}} \qquad ...6.12$$

In some references, s_r, is given the symbol, s_y. The standard deviation of the slope, s_m, is then determined by the equation

$$s_m = \sqrt{\frac{s_r^2}{S_{xx}}} \qquad ...6.13$$

The standard deviation of the intercept, s_b, is determined by the equation

$$s_b = s_r \sqrt{\frac{1}{N - (\sum x_i)^2 / \sum x_i^2}} \qquad \text{...6.14}$$

The derivation of equations 6.12 to 6.14 is elucidated from basic principles by Aikens and co-authors (Aikens et al., 1978).

The standard deviation for results obtained from the calibration curve, s_c, is determined by the equation

$$s_c = \frac{s_r}{m}\sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 S_{xx}}} \qquad \text{...6.15}$$

This equation provides a way of calculating the standard deviation from the mean, $\bar{y}_c$, of a set of M replicate analyses of unknowns when a calibration curve that contains N points is used. In this equation, $\bar{y}$ is the mean of y for N calibration data.

The unknown, x, is then determined from

$$x = \frac{(y \pm s_r) - (b \pm s_b)}{m \pm s_m} \qquad \text{...6.16}$$

The principle of propagation of error (absolute variances in numerator additive, relative variances in denominator in the division step) is borne in mind when x is calculated.

The correlation coefficient is used as a measure of the correlation between two variables. The Pearson correlation coefficient is given by the equation (Christian, 1994):

$$r = \sum \frac{(x_i - \bar{x})(y_i - \bar{y})}{N s_x s_y} \qquad ...6.17$$

where *r* is the correlation coefficient; N is the number of observations; s_x is the standard deviation of *x* and s_y is the standard deviation of *y*. x_i and y_i are the individual values of the variables *x* and y, respectively. For ease of calculation, equation 6.17 is usually written in the form:

$$r = \frac{N\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{[N\sum x_i^2 - (\sum x_i)^2][N\sum y_i^2 - (\sum y_i)^2]}} \qquad ...6.18$$

Generally, a $0.90 < r < 0.95$ indicates a fair curve, $0.95 < r < 0.99$ indicates a good curve, and $r > 0.99$ indicates excellent linearity.

Chapter 7 Ion Selective electrode method – Experimental

7.1 Introduction

In this study, the Ion Selective electrode method is used to determine the amount of fluoride in various treatments of Kynoch and Omnia phosphogypsum samples. The direct calibration method is compared to the normal calibration method in various determinations as a cross check of the stability and calibration of the instrumentation, and thus the validity of the individual results. The study also investigates the effect of the pH control of samples on the recovery of fluoride.

7.2 Instrumentation

A Metrohm 692 pH/Ion Meter with a Metrohm Fluoride ISE 6.0502.150 indicator electrode coupled with Metrohm reference electrode 6.0733.100 were used.

7.3 Chemicals

- TISAB Buffer 1:

Preparation has been described in Section 5.2.4.

- Fluoride stock solution:

2.2196 g NaF (ANALAR grade, BDH) was weighed from a salt which had been previously dried at 115 °C for two hours. It was then transferred to a 1L volumetric flask, dissolved in deionised water and brought up to the mark. The concentration of fluoride in the stock solution was 1000 mg/*l*.

- Fluoride standard solutions:

Various fluoride standard solutions were prepared by serial dilution of the 1000 ppm stock solution.

7.4 Procedure for potential measurements

Using a pipette, an accurately measured volume (usually 20.00 mL) of the standard solution was transferred to a 50 mL plastic beaker. An equal volume of TISAB was added to the standard solution. A polyethylene coated magnetic stirrer bar was placed in the mixture, and the solution was stirred with the aid of a magnetic stirrer. The fluoride indicator electrode and the reference electrode were immersed in the solution, and once the potential had stabilized, the measurement was taken. On average, the potentials stabilized within five minutes. The same procedure was repeated for all standards and samples.

7.5 Procedure for sample analysis

Two methods were used to determine fluoride in Kynoch and Omnia phosphogypsum samples. In the first instance, the direct ion concentration method was utilized. In this case the measuring instrument, the Ion Meter, was calibrated initially and then the concentration of the fluoride ion in each standard or sample was determined directly from the instrument. The Ion Meter was used in the manual mode. Secondly, the normal calibration method was used. The potential for each fluoride standard solution was measured and the calibration curve (E versus log[F^-]) constructed. The fluoride concentration in each sample was determined from the calibration curve. Each sample was analysed in triplicate for each method of analysis mentioned above. The analyses were carried out at ambient temperature. Since the potential is a function of temperature, the temperature of the solutions was measured manually and entered into the Ion Meter program prior to each analysis. At this stage, the emphasis was on the establishment of the stability and the calibration of the instrumentation used for the Ion selective electrode method, hence the samples were limited to Kynoch and Omnia phosphogypsum samples.

7.6 Fluoride content determination in untreated Kynoch phosphogypsum

In the subsequent work, Kynoch (batch 1) phosphogypsum samples were analysed for fluoride content. The phosphogypsum samples were categorized into various batches depending on the time at which each was sourced from the plants. Each specific batch would thus represent a sample obtained from common reaction conditions and same raw materials. The phosphogypsum samples were prepared by the fusion procedure as described in Section 5.2.3. The pH of each sample solution was adjusted to a value between 5 and 6 (Javellana and Jawed, 1981). The results were reported and statistical analysis performed on each sample.

7.6.1 Samples

- **Sample 1**

A Kynoch sample weighing 0.6270g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The pH of the sample was adjusted to 5.1. The sample was made up to 250 mL.

The samples were analysed in triplicate and the preparation data for each sample has been summarized in Table 7.1

Table 7.1: Kynoch sample data

Sample	Sample mass	Mass ZnO	Mass Na_2CO_3	pH	Final Volume
No.1	0.6270g	0.5g	2.5g	5.1	250 mL
No.2	0.6254g	0.5g	2.5g	5.1	250 mL
No.3	1.2528g	1.0g	5.0g	5.1	500 mL

7.6.2 Results

The results obtained are tabulated in Tables 7.2, 7.3 and 7.4.

Table 7.2: Results for the direct ion concentration mode for Kynoch batch 1

Kynoch sample	[F⁻] (ppm) for each replicate
Sample 1	3.13; 3.10; 3.10
Sample 2	2.92; 2.96; 2.92
Sample 3	2.66; 2.68; 2.66

Table 7.3: Results for fluoride standards (normal calibration method)

Fluoride standard	[F⁻] (ppm)	Potential (mV)
Standard 1	5.0×10^{-4}	228.4
Standard 2	5.0×10^{-2}	163.8
Standard 3	0.25	123.7
Standard 4	0.50	106.3
Standard 5	2.50	65.6

Table 7.4: Results for the normal calibration method for Kynoch batch 1

Kynoch sample	Potential (mV) for each replicate
Sample 1	77.6; 77.6; 77.6
Sample 2	79.3; 78.8; 79.3
Sample 3	81.6; 81.5; 81.4

7.6.3 Discussion of results for the direct ion measurement method

- **Sample 1**

The sample standard deviation for the first replicate was computed to be 0.02 ppm, using equation 6.2. Hence, the average fluoride ion concentration $[F^-]_{ave}$ = 3.11 ± 0.02 ppm. The relative standard deviation (RSD) was found to be 0.5% using equation 6.3.

The results for the determination of standard deviation, average concentration of fluoride and the RSD were determined for the other two replicates in a similar fashion as for sample 1 above and summarised in Table 7.5.

Table 7.5: Fluoride concentration results for the direct ion concentration mode for Kynoch batch 1

Sample	$[F^-]_{ave}$
Sample 1	3.11 ± 0.02 ppm, RSD = 0.5%
Sample 2	2.93 ± 0.02 ppm, RSD = 0.8%.
Sample 3	2.67 ± 0.01 ppm, RSD = 0.4%.

The mean concentration of fluoride for the entire set of results was determined using equation 6.1 and found to be 2.90 ppm. The sample standard deviation for the results was 0.22 ppm. The pooled standard deviation for the method was determined as described in Section 6.2.4, using equation 6.4., and found to be 0.02 ppm. The two extreme data points in the entire set of results, 2.66 and 3.13 ppm, were tested using equation 6.5 for the Q-test and found to be valid at 99% confidence level.

Percentage fluoride:

- **Sample 1**

$$[F^-] = 3.13\,ppm\ for\ first\ replicate\ (Table\ 7.2)$$

$$\%F^- = \frac{3.13\,mg/L \times 0.250L \times 10^{-3}\,g/mg \times 100\%}{0.6270}$$

$$= 0.125\%$$

A similar calculation for the second replicate yielded 0.124% F^- and the third replicate gave 0.124% F^-. The average value for the set was 0.124 ± 0.001% F^- with RSD of 0.46%.

The results for the determination of percentage fluoride in the second and third samples were computed in a similar way and summarised in Table 7.6:

Table 7.6: % Fluoride for the direct ion concentration mode for Kynoch batch 1

Sample	% $[F^-]$	% $[F^-]_{ave}$
Sample 1	0.125; 0.124; 0.124	0.124 ± 0.001% F^-, RSD = 0.46%
Sample 2	0.117; 0.118; 0.117	0.117 ± 0.001% F^-, RSD = 0.49%.
Sample 3	0.106; 0.107; 0.106	0.106 ± 0.001% F^-, RSD = 0.54%.

The mean F^- percentage for the entire set of results was 0.116%. The sample standard deviation for the results was 0.009%.

7.6.4 Analysis of results by the normal calibration method

The results were plotted in Figure 7.1as potential (mV) versus log $[F^-]$. A careful analysis of this plot clearly indicates that there is a linear part at higher fluoride concentration and a non-linear part at low fluoride concentrations. The linear range is between the fluoride standard concentration of 0.05 and 2.50 ppm. The low fluoride standard concentration of 0.0005 ppm is in the non-linear part of the curve. The non-linear part of the calibration curve would require that a substantial number of data points be taken in this area to enable a more accurate interpolation if this area of the curve must be used in the determination of amount of fluoride in the sample. However, this was not necessary in this case. On this basis, regression analysis, described in Section 6.2.6, was utilised for derivation of the equation for the best straight line for data that was within the linear range (0.05 – 2.50 ppm F^-) of the calibration curve. Utilizing the least square method, the equation for the best straight line is,

$$E = -57.8\log[F^-] + 88.75$$

where E is the measured potential (mV) of the solution and $[F^-]$ is the fluoride concentration (ppm).

The standard deviations about the least squares line were computed using equations 6.12, 6.13 and 6.14. The standard deviation, s_r, about the regression was 0.21. The standard deviations about the slope, s_m, and of the intercept, s_b, were 0.17 and 0.13 respectively. The correlation coefficient was calculated using equation 6.16 and found to be 1.00.

Concentration of fluoride:

- **Sample 1**

The first replicate produced a potential of 77.6 mV. Therefore, using the above equation, fluoride concentration in dilute solution analysed was

$$\log[F^-] = \frac{77.6 - 88.75}{-57.8}$$

$$\therefore \quad [F^-] = 1.559\, ppm$$

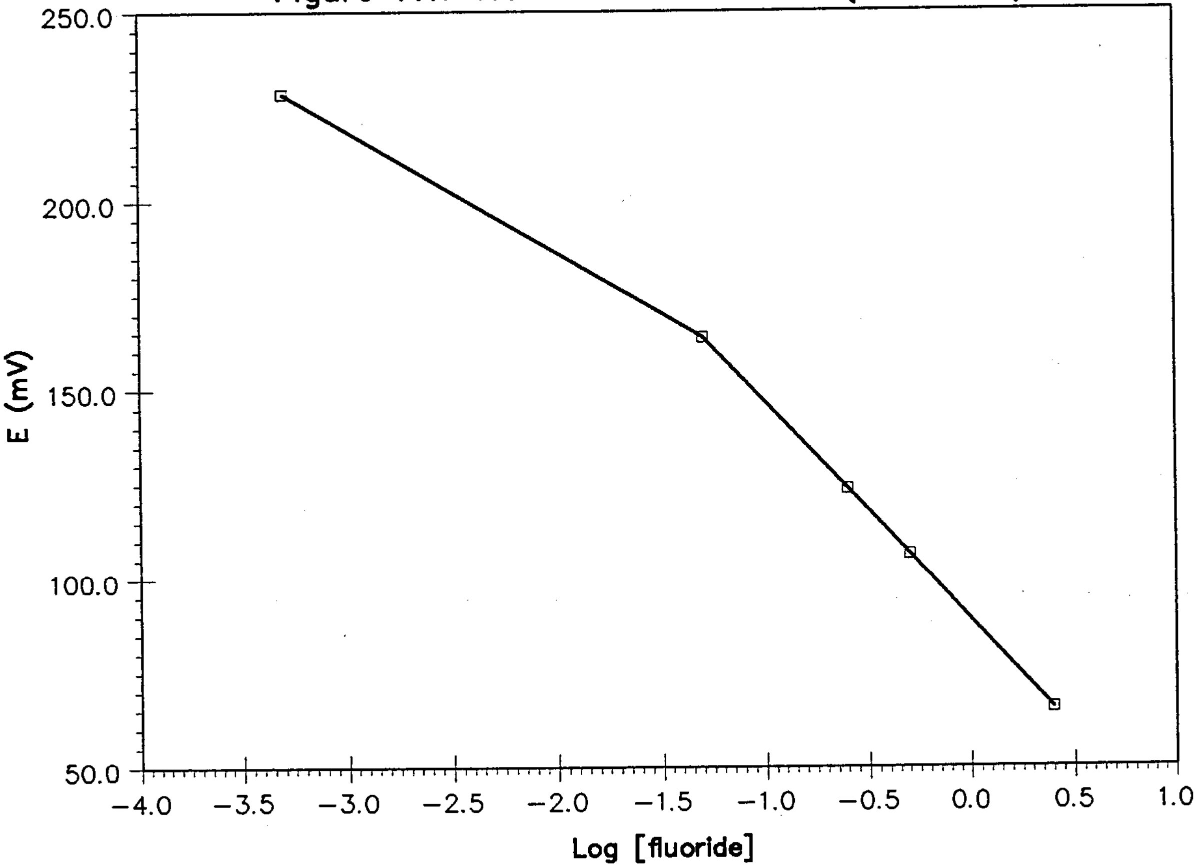


Figure 7.1: ISE calibration curve (Raw data)

Taking account of the dilution factor, the concentration of fluoride in the original solution was,

$$[F^-]_{sample} = \frac{1.559\,ppm \times 40.00\,mL}{20.00\,mL}$$

$$= 3.118 \approx 3.12\,ppm$$

A similar calculation for the second replicate gave $[F^-]$ =3.131 ≈ 3.13 ppm. The result for the third replicate was found to be $[F^-]$ =3.118 ≈ 3.12 ppm. The mean concentration was 3.12 ±0.01 ppm with RSD of 0.24%.

The results for the second and the third samples were treated in a similar manner as done for the first sample above. The results are summarised in Table 7.7.

Table 7.7: Fluoride concentration results for the normal calibration method for Kynoch batch 1

Sample	$[F^-]_{ave}$
Sample 1	3.12 ± 0.01 ppm, RSD = 0.24%
Sample 2	2.93 ± 0.03 ppm, RSD = 1.1%.
Sample 3	2.67 ± 0.01 ppm, RSD = 0.4%.

The pooled standard deviation (using equation 6.4)for the method was 0.02ppm F^-. The mean fluoride concentration for the entire set of results was 2.91 ppm. The sample standard deviation for the results was 0.23 ppm.

Percentage fluoride:

- **Sample 1**

$$[F^-] = 3.13\,ppm\ for\ first\ replicate$$

$$\%F^- = \frac{3.13\,mg/L \times 0.250\,L \times 10^{-3}\,g/mg \times 100\%}{0.6270}$$

$$= 0.125\%$$

A similar calculation for the second replicate yielded 0.125%F^- and the third replicate gave 0.124%F^-. The average value for the set was 0.125 ± 0.001%F^- with RSD of 0.46%.

The percentage of fluoride contained in the second and third samples was calculated as shown above and the results summarised in Table 7.8.

Table 7.8: % Fluoride for the normal calibration method for Kynoch batch 1

Sample	% [F^-]	% [F^-]$_{ave}$
Sample 1	0.125; 0.125; 0.124	0.125 ± 0.001% F^-, RSD = 0.46%
Sample 2	0.117; 0.118; 0.117	0.117 ± 0.002% F^-, RSD = 1.5%.
Sample 3	0.106; 0.107; 0.106	0.107 ± 0.002% F^-, RSD = 0.54%.

The mean percentage for the entire set of results for samples 1, 2 and 3 was 0.116%F^-. The sample standard deviation for the results was 0.009%F^-. The results of the analysis of the Kynoch phosphogypsum sample are summarised in Table 7.9.

Table 7.9: Overall results for the analysis of the Kynoch batch 1sample.

Direct Ion Determination method	Normal Calibration method
% F^- = 0.116 ± 0.009	% F^- = 0.116 ± 0.009

7.6.5 Conclusion

The analysis methods which were used in this determination, namely, direct ion measurement method and the normal calibration method, yielded practically the same results as shown in Table 7.9. However, the calibration curve for the normal calibration method (Figure 7.1) deviates from linearity at low fluoride ion concentrations. Hence, the direct ion method could prove to be erratic at very low concentrations of the fluoride ion. The average amount of fluoride, as determined by direct ion method and the normal calibration method, is 0.116% in Kynoch phosphogypsum. The enormous advantages of the direct ion method are that it is relatively fast, it does not need many calibration data points and it can be automated with a view to on-line analysis.

7.7 Fluoride content determination in untreated Omnia phosphogypsum

Omnia phosphogypsum samples (batch 1) were analysed to determine the levels of fluoride. The results for each replicate were reported and statistically analysed. The phosphogypsum samples were prepared by the fusion procedure as described in Section 5.2.3.

7.7.1 Samples

- **Sample 1**

An Omnia sample weighing 0.6248g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The pH was adjusted to 5.1 with concentrated nitric acid. The sample was made up to 250 mL with deionised water.

The samples were analysed in triplicate and the preparation data for each sample has been summarized in Table 7.10

Table 7.10: Omnia sample data

Sample	Sample mass	Mass ZnO	Mass Na_2CO_3	pH	Final Volume
No.1	0.6248g	0.5g	2.5g	5.1	250 mL
No.2	1.2538g	1.0g	5.0g	5.2	500 mL
No.3	0.6242g	0.5g	2.5g	5.1	250 mL

7.7.2 Results

The results obtained are tabulated in Table 7.11, Table 7.12 and Table 7.13

Table 7.11: Results for the direct ion concentration mode for Omnia batch 1.

Omnia sample	[F$^-$] (ppm) for each replicate
Sample 1	1.32; 1.29; 1.30
Sample 2	1.07; 1.05; 1.05
Sample 3	0.988; 0.986; 0.986

Table 7.12: Results for fluoride standards (normal calibration method)

Fluoride standard	[F$^-$] (ppm)	Potential (mV)
Standard 1	0.010 ppm	207.8
Standard 2	0.050 ppm	180.0
Standard 3	0.125 ppm	156.8
Standard 4	0.250 ppm	139.2
Standard 5	0.500 ppm	121.3
Standard 6	2.50 ppm	80.9

Table 7.13: Results for the normal calibration method for Omnia batch 1.

Omnia sample	Potential (mV) for each replicate
Sample 1	116.1; 116.2; 116.1
Sample 2	120.4; 120.7; 120.8
Sample 3	122.6; 122.6; 122.1

7.7.3 Discussion of results for the direct Ion measurement method

- **Sample 1**

The sample standard deviation for the three replicates was computed to be 0.02

ppm. Hence, the average fluoride ion concentration $[F^-]_{ave}$ = 1.30 ± 0.02 ppm. The relative standard deviation (RSD) was calculated to be 1.1%.

The results for the determination of standard deviation, average concentration of fluoride and the RSD were determined for the other two samples analysed in the same manner as done for sample 1 above and summarised in Table 7.14.

Table 7.14: Fluoride concentration results for the direct ion concentration mode for Omnia batch 1

Sample	$[F^-]_{ave}$
Sample 1	1.30 ± 0.02 ppm, RSD = 1.1%
Sample 2	1.06 ± 0.01 ppm, RSD = 1.1%.
Sample 3	0.99 ± 0.01 ppm, RSD = 0.7%.

For samples 1, 2, and 3 the mean concentration of fluoride was 1.12 ppm. The sample standard deviation was found to be 0.16 ppm. The pooled standard deviation for the method was computed to be 0.01 ppm from equation 6.4.

The quantity of fluoride in the samples was determined as percentage fluoride as follows:

- **Sample 1**

$$[F^-] = 1.32\, ppm\ for\ first\ replicate\ (Table\ 7.11)$$

$$\%F^- = \frac{1.32\, mg/L \times 0.250L \times 10^{-3}\, g/mg \times 100\%}{0.6248}$$

$$= 0.0528\% \approx 0.053\%$$

A similar calculation for the second replicate yielded 0.052% and the third replicate yielded 0.052%. The average value for the set was 0.052 ± 0.001%F^- with RSD of 1.1%.

The fluoride amount expressed as percentage, was determined for sample 2 and sample 3 in the same manner as done for sample 1 above. The results are tabulated in Table 7.15.

Table 7.15: % Fluoride for the direct ion concentration mode for Omnia batch 1

Sample	% $[F^-]$	% $[F^-]_{ave}$
Sample 1	0.053; 0.052; 0.052	0.052 ± 0.001% F^-, RSD = 1.1%
Sample 2	0.043; 0.042; 0.042	0.042 ± 0.001% F^-, RSD = 1.1%.
Sample 3	0.040; 0.040; 0.040	0.040 ± 0.000% F^-, RSD = 0.15%.

The mean percentage of fluoride ion for the entire set of results (samples 1 to 3) was 0.045%F^-. The sample standard deviation was found to be 0.006%F^-.

7.7.4 Discussion of results for the normal calibration method

The raw data were plotted on Figure 7.2 as potential (mV) versus log $[F^-]$. Clearly, the linear range of the curve is between 0.05 to 2.50 ppm F^-. The data point for the 0.01 ppm fluoride standard was outside of the linear range. Regression analysis was used to derive calibration data, using only the data points that fell within the linear range. On utilizing the least square method (Section 6.2.6), the equation for the least squares line was

$$E = -58.3894\log[F^-] + 103.9988$$

where E is the potential (mV) of the solution and [F⁻] is the fluoride concentration (ppm).

The standard deviation, s_r, about the regression was 0.18. The standard deviations about the slope, s_m, and of the intercept, s_b, were 0.14 and 0.11 respectively. The correlation coefficient was calculated using equation 6.16 and found to be 1.00.

The concentration of fluoride in each sample was then determined from the measured potentials as follows:

- **Sample 1**

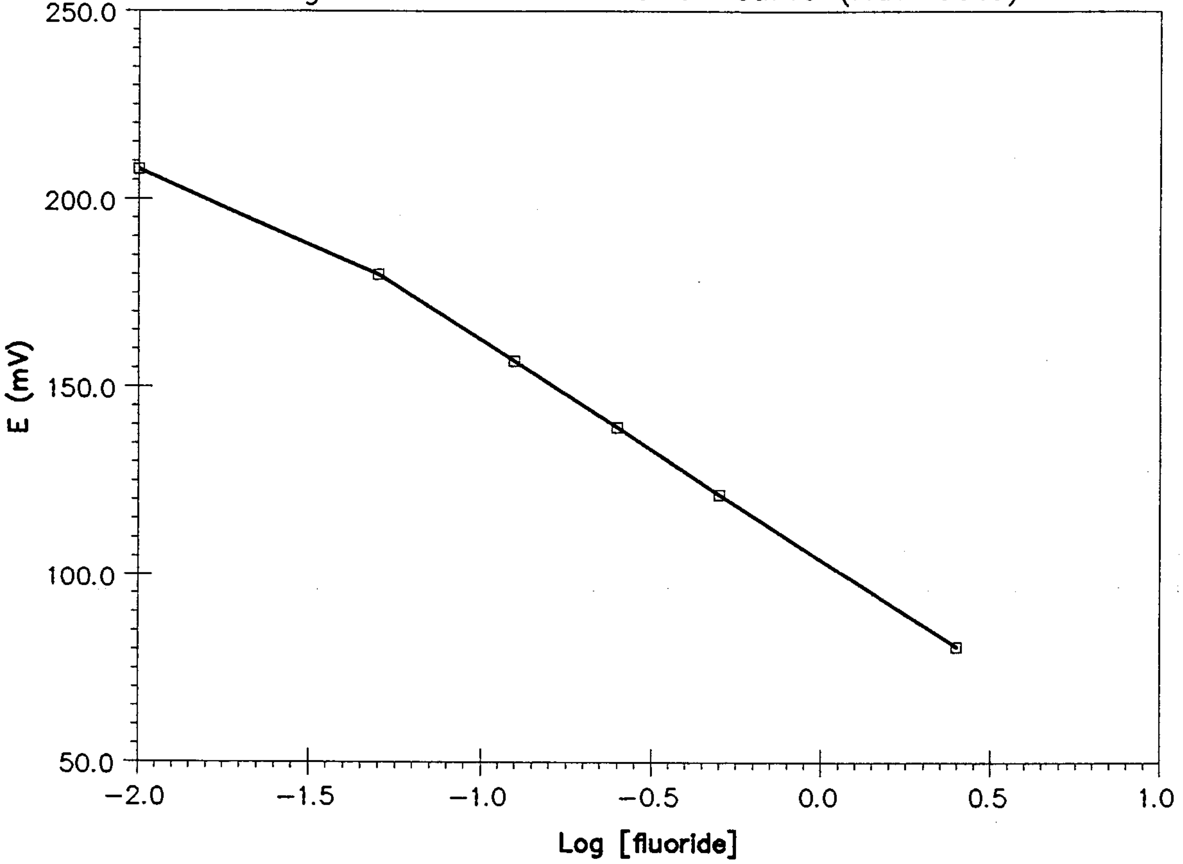
The first replicate had a potential of 116.1 mV. Substituting into the least squares line equation, fluoride ion concentration in the diluted sample was determined as

$$\log[F^-] = \frac{116.1 - 103.9988}{-58.3894}$$
$$\therefore [F^-] = 0.6205\,ppm$$

For the analysis of the Omnia sample, the volume of aliquot taken was 10.00 mL as was the volume of TISAB. Taking account of the dilution factor, the fluoride concentration in the original sample was

$$[F^-]_{sample} = \frac{0.6205\,ppm \times 20.00\,mL}{10.00\,mL}$$
$$= 1.241 \approx 1.24\,ppm$$

Figure 7.2: ISE calibration curve (Raw data)



A similar calculation for the second replicate gave $[F^-] = 1.236 \approx 1.24$ ppm. The result for the third replicate was found to be $[F^-] = 1.241 \approx 1.24$ ppm. The mean concentration was 1.24 ±0.00 ppm with RSD of 0.23%.

The concentration of fluoride in sample 2 and sample 3 were determined in a similar way as done for sample 1 above. The results are summarised in Table 7.16.

Table 7.16: Fluoride concentration results for the normal calibration method for Omnia batch 1

Sample	$[F^-]_{ave}$
Sample 1	1.24 ±0.00 ppm, RSD = 0.23%
Sample 2	1.04 ±0.01 ppm, RSD = 0.8%.
Sample 3	0.97 ±0.01 ppm, RSD = 1.2%.

The mean fluoride concentration for the entire set of results was 1.08 ppm. The sample standard deviation was 0.14 ppm.

The quantity of fluoride in the samples was determined as percentage fluoride as follows:

- **Sample 1**

$$[F^-] = 1.241\,ppm$$

$$\%F^- = \frac{1.241\,mg/L \times 0.250L \times 10^{-3}\,g/mg \times 100\%}{0.6248\,g}$$

$$= 0.04948\% \approx 0.049\%$$

A similar calculation for the second and third replicates yielded 0.049% F^- and 0.049%F^- respectively. The average fluoride concentration for the set was 0.049% with RSD of 0.02%.

A similar calculation was followed for the computation of the percentage fluoride contained in sample 2 and sample 3 and the results tabulated in Table 7.17.

Table 7.17: % Fluoride for the normal calibration method for Omnia batch 1

Sample	% [F^-]	% [F^-]$_{ave}$
Sample 1	0.049; 0.049; 0.049	0.049 ± 0.000% F^-, RSD = 0.02%
Sample 2	0.042; 0.041; 0.041	0.041 ± 0.001% F^-, RSD = 0.87.
Sample 3	0.038; 0.038; 0.039	0.038 ± 0.001% F^-, RSD = 1.3%.

The mean percentage fluoride for the entire set of results was 0.043%. The sample standard deviation was determined to be 0.006%. The results for the analysis of Omnia phosphogypsum are summarised in Table 7.18.

Table 7.18: Overall results for the analysis of Omnia phosphogypsum

Direct Ion Determination method	Normal Calibration method
% F^- = 0.045% ± 0.006	% F^- = 0.043% ± 0.006

7.7.5 Conclusion

In the analysis of the Omnia phosphogypsum batch 1 sample, the direct ion measurement method and the normal calibration method yielded similar results, as shown in Table 7.18. The average amount of fluoride in Omnia phosphogypsum was 0.044% for each of the two analysis methods.

7.8 Determination of fluoride content in sulphuric acid treated Kynoch and Omnia phosphogypsum

7.8.1 Introduction

In the following experiments, Kynoch batch 1and Omnia batch 1 phosphogypsum samples were treated with sulphuric acid in order to leach out the fluoride. The method followed by Jarosiński was adapted as explained in Section 4.4 (Jarosiński, 1994).

7.8.2 Sulphuric acid treated Kynoch phosphogypsum

The sulphuric acid treated Kynoch phosphogypsum samples were labelled KYN2SUL-GH4 for identification purposes. The samples were prepared by the fusion method as described in Section 5.2.3. Each sample was analysed in triplicate.

7.8.2.1 Samples

- **Sample 1**

A Kynoch sample weighing 0.6251g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The pH was adjusted to 5.1 with concentrated nitric acid. The sample was made up to 250 mL with deionised water.

The samples were analysed in triplicate and the preparation data for each sample has been summarized in Table 7.19.

Table 7.19: Sulphuric acid treated Kynoch sample data

Sample	Sample mass	Mass ZnO	Mass Na_2CO_3	pH	Final Volume
No.1	0.6251g	0.5g	2.5g	5.1	250 mL
No.2	1.2495g	1.0g	5.0g	5.1	500 mL
No.3	0.6264g	0.5g	2.5g	5.1	250 mL

7.8.2.2 Procedure for potential measurements

An accurately measured volume (usually 10.00 mL) of the sample or standard was transferred into a 50 mL plastic beaker. An equal volume of TISAB was added to the sample or standard solution. A polyethylene coated magnetic stirrer bar was placed in the mixture and the solution was stirred by a magnetic stirrer. The fluoride indicator electrode and the reference electrode were immersed in the solution, and once the potential had stabilized, the measurement was taken. On average, the potentials stabilized within five minutes.

7.8.2.3 Procedure for sample analysis

The direct ion concentration method and the normal calibration method were used to determine the fluoride in each of the samples. The procedure followed has been described in Section 7.5.

7.8.2.4 Results for sulphuric acid treated Kynoch phosphogypsum

The results for sulphuric acid treated Kynoch phosphogypsum are given in Table 7.20 (direct ion measurement method), Tables 7.21 and 7.22 (normal calibration method). Close examination of results obtained for the potentials of various fluoride ion standards (Table 7.21) indicates some differences to the results for the same concentrations of fluoride ion standards obtained previously (Table 7.12). This is because the Ion Meter used does not have an inbuilt baseline zeroing facility. Hence, it is necessary to calibrate the instrument on a routine basis.

Table 7.20: Results for the direct ion concentration mode for KYN2SUL-GH4 sample

KYN2SUL-GH4 sample	[F$^-$] (ppm) for each replicate
Sample 1	0.241; 0.243; 0.238
Sample 2	0.259; 0.262; 0.259
Sample 3	0.260; 0.264; 0.261

Table 7.21: Results for fluoride standards (normal calibration method)

Fluoride standard	[F$^-$] (ppm)	Potential (mV)
Standard 1	0.050 ppm	175.8
Standard 2	0.125 ppm	156.5
Standard 3	0.250 ppm	139.4
Standard 4	0.500 ppm	121.9
Standard 5	2.50 ppm	81.0

Table 7.22: Results for the normal calibration method for KYN2SUL-GH4 sample

KYN2SUL-GH4 sample	Potential (mV) for each replicate
Sample 1	155.4; 155.5; 155.4
Sample 2	154.4; 154.4; 155.4
Sample 3	155.4; 155.3; 155.3

7.8.2.5 Discussion of results for the direct ion measurement method for KYN2SUL-GH4

- **Sample 1**

The sample standard deviation was computed to be 0.003 ppm F^-. Hence, the fluoride ion concentration $[F^-]_{ave}$ = 0.241 ± 0.003 ppm. The relative standard deviation (RSD) was 1.05%.

The results for the determination of standard deviation, average concentration of fluoride and the RSD were determined for the other two samples and summarised in Table 7.23.

Table 7.23: Fluoride concentration results for the direct ion measurement method for KYN2SUL-GH4

Sample	$[F^-]_{ave}$
Sample 1	0.241 ± 0.003 ppm, RSD = 1.05%
Sample 2	0.260 ± 0.002 ppm, RSD = 0.7%.
Sample 3	0.262 ± 0.002 ppm, RSD = 0.8%.

For the entire set of results, the mean concentration of fluoride was 0.254 ppm. The sample standard deviation was 0.012 ppm. The pooled standard deviation for the method was 0.002 ppm as determined from equation 6.4.

The quantity of fluoride in the samples was determined as a percentage as follows:

- **Sample 1**

$$[F^-] = 0.241\, ppm\ for\ first\ replicate\ (Table\, 7.20)$$

$$\%F^- = \frac{0.241 mg/L \times 0.250 L \times 10^{-3} g/mg \times 100\%}{0.6251}$$

$$= 0.00964\% \approx 0.010\%$$

A similar calculation for the second replicate yielded 0.010% F^- and the third replicate gave 0.010% F^-. The average value for the set was 0.010 ± 0.000% F^- with RSD of 1.05%.

A similar calculation was followed for the computation of the percentage fluoride contained in sample 2 and sample 3 and the results tabulated in Table 7.24.

Table 7.24: % Fluoride for the direct ion mode for KYN2SUL-GH4

Sample	% $[F^-]$	% $[F^-]_{ave}$
Sample 1	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 1.0%
Sample 2	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 0.6%
Sample 3	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 0.6%

The mean percentage for the entire set of results was 0.010%F^-. The sample standard deviation was 0.000%F^-.

7.8.2.6 Analysis of results obtained by the normal calibration method for KYN2SUL-GH4

The raw data were plotted on Figure 7.3 as potential (mV) versus log [F^-]. All the raw data points were included in the derivation of the least squares, in line with the observation made from Section 7.7.4 that the linear range should include the limits between 0.05 to 2.50 ppm F^-. Using the least square method (Section 6.2.6), the equation for the least squares line was

$$E = -56.25\log[F^-] + 104.44$$

where E is the potential (mV) measured with the ISE and [F^-] is the fluoride concentration (ppm).

The standard deviation, s_r, about the regression was 1.58. The standard deviations about the slope, s_m, and of the intercept, s_b, were 1.23 and 0.97 respectively. The correlation coefficient was calculated using equation 6.16 and found to be 1.00.

The concentration of fluoride in each sample was then determined from the measured potentials and given below.

- **Sample 1**

After consideration of the dilution effects, the fluoride content for the three replicates was 0.248 ppm; 0.247 ppm and 0.248 ppm respectively. The mean concentration was 0.248 ±0.001 ppm F^- with RSD of 0.23%.

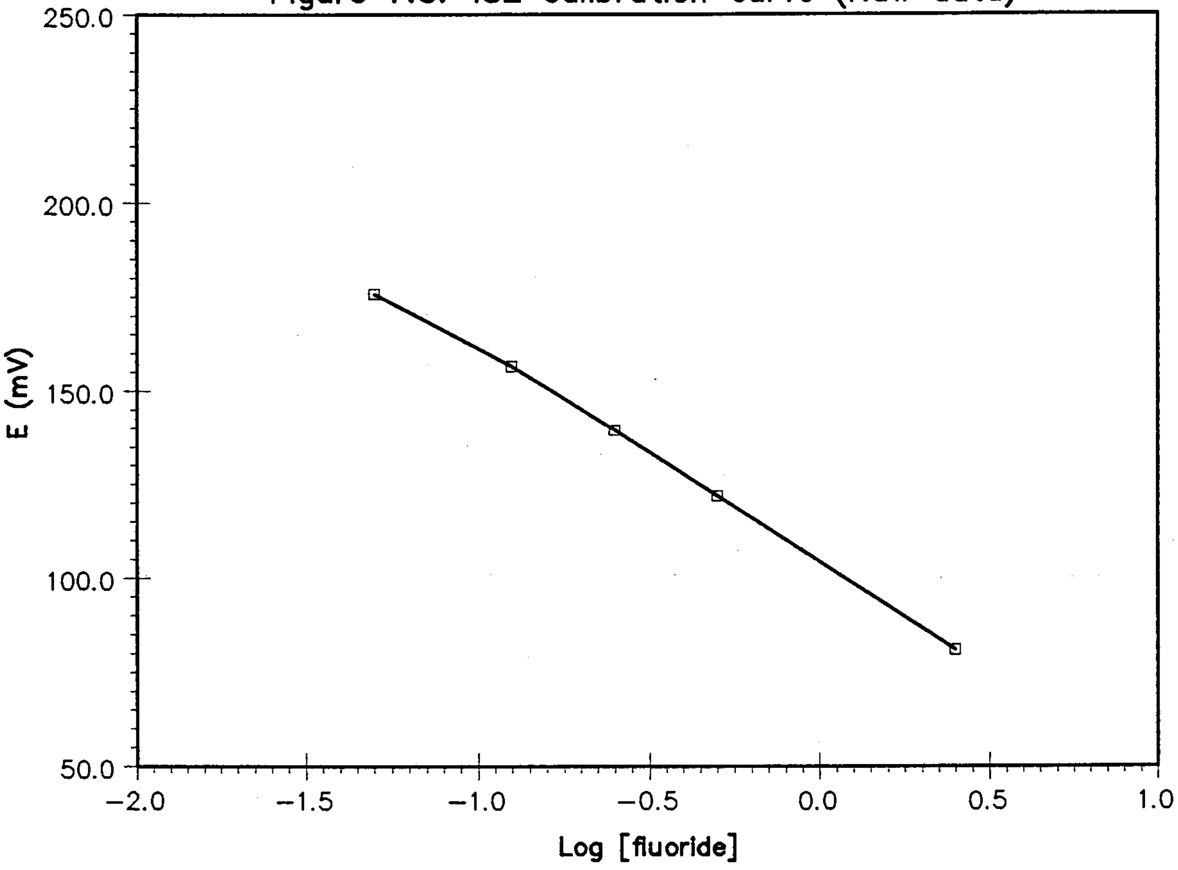


Figure 7.3: ISE calibration curve (Raw data)

The concentration of fluoride contained in the other two samples (sample 2 and sample 3) were determined in the same way as for sample 1. The results are given in Table 7.25.

Table 7.25: Fluoride concentration results for the normal calibration method for KYN2SUL-GH4

Sample	$[F^-]$ ppm	$[F^-]_{ave}$
Sample 1	0.248; 0.247; 0.248	0.248 ±0.001 ppm, RSD = 0.23%
Sample 2	0.259; 0.259; 0.248	0.255 ±0.006 ppm F^-, RSD = 2.5%.
Sample 3	0.248; 0.249; 0.249	0.249 ±0.001 ppm F^-, RSD = 0.23%.

The mean fluoride concentration for the entire set of results was 0.251 ppm. The sample standard deviation was 0.004 ppm.

The quantity of fluoride in the samples was determined as percentage fluoride, as described above, and the results are given below.

- **Sample 1**

Fluoride content was calculated for each of the three replicates as: 0.010%; 0.010%; 0.010% respectively. The average value for the set was 0.010 ± 0.000%F^- with RSD of 0.23%.

The results of the percentage fluoride contained in each of the three samples analysed are tabulated in Table 7.26.

Table 7.26: % Fluoride for the normal calibration method for KYN2SUL-GH4

Sample	% $[F^-]$	% $[F^-]_{ave}$
Sample 1	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 0.23%
Sample 2	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 2.7%
Sample 3	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 0.55%

The mean fluoride percentage for the entire set of results was 0.010%. The sample standard deviation was 0.000%F^-.

The results obtained by the two analysis methods (direct ion method and normal calibration method) have been summarised in Table 7.27.

Table 7.27: Overall results for the analysis of the **KYN2SUL-GH4** sample.

Direct Ion Determination method	Normal Calibration method
% F^- = 0.010 ± 0.000%	% F^- = 0.010 ± 0.000%

7.8.2.7 Conclusion

The two methods of analysis which were used for the determination of fluoride concentration, namely the direct ion measurement method and the normal calibration method, yielded statistically close results, as shown in Table 7.27. Of the original amount of fluoride, 91 % was leached out. The amount of fluoride that can be accepted for the use of phosphogypsum as set retarder in the cement industry should not exceed 0.2% (Jarosiński, 1994). The amount of fluoride obtained in the sulphuric acid treated Kynoch phosphogypsum was 0.01%. Hence, the sulphuric acid purification method was very effective.

7.8.3 Determination of fluoride content in sulphuric acid treated Omnia phosphogypsum

The Omnia batch 1 phosphogypsum was purified as explained in Section 4.4. The sulphuric acid purified sample was labelled OM2SUL-GH4. In order to carry out statistical analysis, samples were prepared as explained in the method procedure in Section 5.2.3.

7.8.3.1 Samples

- **Sample 1**

An Omnia sample weighing 0.6248g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The pH was adjusted to 5.1 with concentrated nitric acid. The sample was made up to 250 mL with deionised water.

The samples were analysed in triplicate and the preparation data for each sample has been summarized in Table 7.28

Table 7.28: Omnia sample data

Sample	Sample mass	Mass ZnO	Mass Na_2CO_3	pH	Final Volume
No.1	0.6248g	0.5g	2.5g	5.1	250 mL
No.2	1.2503g	1.0g	5.0g	5.2	500 mL
No.3	0.6286g	0.5g	2.5g	5.1	250 mL

7.8.3.2 Procedure for potential measurements

An accurately measured volume of the sample or standard (usually 10.00 mL) was transferred to a 50 mL plastic beaker. An equal volume of TISAB was added. The procedure explained in Section 7.4 was followed.

7.8.3.3 Procedure for sample analysis

The direct ion concentration method and the normal calibration method were used to determine the fluoride in each of the samples. The procedure followed has been described in Section 7.5.

7.8.3.4 Results

The results of the direct ion concentration method are given in Table 7.29, and the results of the normal concentration method in Tables 7.30 and 7.31.

Table 7.29: Results of the direct ion concentration method for OM2SUL-GH4 sample

OM2SUL-GH4 sample	[F$^-$] (ppm) for each replicate
Sample 1	0.249; 0.246; 0.251
Sample 2	0.332; 0.337; 0.331
Sample 3	0.336; 0.340; 0.339

Table 7.30: Results of fluoride standards (normal calibration method)

Fluoride standard	[F$^-$] (ppm)	Potential (mV)
Standard 1	0.500 ppm	121.2
Standard 2	0.250 ppm	138.5
Standard 3	0.125 ppm	152.2
Standard 4	0.050 ppm	178.8
Standard 5	0.010 ppm	213.4
Standard 6	0.001 ppm	228.1

Table 7.31: Results of the normal calibration method for OM2SUL-GH4 sample

OM2SUL-GH4 sample	Potential (mV) for each replicate
Sample 1	153.3; 153.7; 154.0
Sample 2	147.6; 147.8; 147.9
Sample 3	147.9; 147.9; 148.0

7.8.3.5 Discussion of results of the direct ion measurement method for OM2SUL-GH4

- **Sample 1**

The sample standard deviation for the first replicate was computed to be 0.003 ppm F$^-$. Hence, the fluoride ion concentration $[F^-]_{ave} = 0.249 \pm 0.003$ ppm. The relative standard deviation (RSD) was 1%.

The second and third samples were treated in the same way as sample 1 and the results summarised in Table 7.32.

Table 7.32: % Fluoride for the direct ion mode for OM2SUL-GH4

Sample	$[F^-]$ ppm	$[F^-]_{ave}$
Sample 1	0.249; 0.246; 0.251	0.249 ± 0.003 ppm, RSD = 1.0%
Sample 2	0.332; 0.337; 0.331	0.333 ± 0.003 ppm, RSD = 1.0%
Sample 3	0.336; 0.340; 0.339	0.338 ± 0.002, RSD = 0.6%

For the entire set of results, the mean concentration of fluoride was 0.307 ppm. The sample standard deviation was 0.050 The pooled standard deviation for the method was computed to be 0.003 ppm F^- from equation 6.4.

The quantity of fluoride in the samples was determined as percentage fluoride as previously described. The results for each sample are given below:

- **Sample 1**

The fluoride percentages for each replicate were computed to be: 0.010%; 0.010% and 0.010% respectively. The average fluoride concentration for the set was 0.010 ± 0.000%F^- with RSD of 1.0%.

The percentage composition of sample 2 and sample 3 were similarly determined and the results summarised in Table 7.33.

Table 7.33: % Fluoride for the direct ion mode for OM2SUL-GH4

Sample	% $[F^-]$	% $[F^-]_{ave}$
Sample 1	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 1.0%
Sample 2	0.013; 0.013; 0.013	0.013 ± 0.000% F^-, RSD = 1.0%
Sample 3	0.013; 0.013; 0.013	0.013 ± 0.000% F^-, RSD = 0.6%

The mean fluoride percentage for the entire set of results was 0.012%. The sample standard deviation was 0.002%F^-.

The results are summarized in Table 7.36.

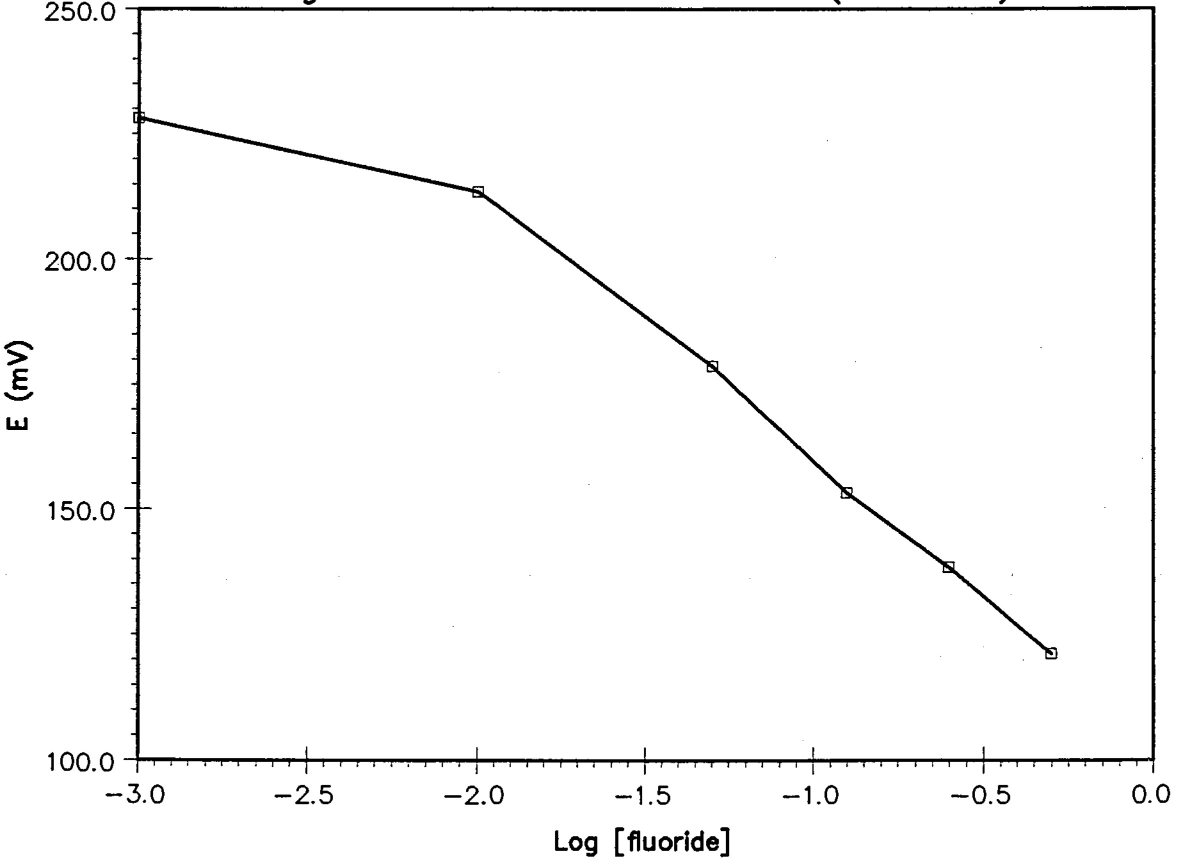
7.8.3.6 Analysis of results obtained by the normal calibration method for OM2SUL-GH4

The results for sulphuric acid treated Omnia phosphogypsum were given in Table 7.30 (standards) and Table 7.31 (samples). It should be noted that in this particular instance the concentrations of the fluoride standards were at the lower ends (0.500 - 0.00100 ppm F^-) when compared to the previous cases. The reason for using lower fluoride concentrations was that an even lower amount of fluoride was expected in the sulphuric acid purified Omnia samples. For instance, in the previous case of the sulphuric acid purified Kynoch phosphogypsum samples (Section 7.8.2.4), the fluoride standards concentration were within the limits 2.50 - 0.0500 ppm. Indeed, the raw data calibration curve (Figure 7.4) indicated that a good linear curve would be obtained by plotting data points within the limits 0.500 - 0.0100 ppm F^-. On utilizing the least square method, the equation obtained for the least squares line was

$$E = -\ 54.68 \log[F^-] + 104.96$$

where E is the potential (mV) measured and $[F^-]$ is the fluoride concentration (ppm). The standard deviation, s_r, about the regression was 2.09. The standard deviations about the slope, s_m, and of the intercept, s_b, were 1.59 and 1.87 respectively. The correlation coefficient was calculated using equation 6.16 and found to be 1.00.

Figure 7.4: ISE calibration curve (Raw data)



The concentration of fluoride in each sample was then determined from the measured potentials as described above.

- **Sample 1**

Using the above equation for the least squares line, the fluoride ion concentration in the dilute solution was determined as 0.130 ppm.

Taking account of the dilution factor, the concentration of fluoride ion in the original sample solution was 0.261 ppm. A similar calculation for the second and third replicates gave fluoride ion concentrations of 0.257 ppm and 0.254 ppm, respectively. The mean concentration was 0.257 ±0.004 ppm F^- with RSD of 1.6%.

The fluoride concentrations of replicates of sample 2 and sample 3 were similarly determined and the results summarised in Table 7.34.

Table 7.34: Fluoride concentration results for the normal calibration method for OM2SUL-GH4

Sample	$[F^-]$ ppm	$[F^-]_{ave}$
Sample 1	0.261; 0.257; 0.254	0.257 ±0.004 ppm, RSD = 1.6%
Sample 2	0.332; 0.329; 0.328	0.330 ±0.002 ppm, RSD = 0.6%.
Sample 3	0.329; 0.329; 0.327	0.328 ±0.001 ppm F^-, RSD = 0.4%.

The mean fluoride concentration for the entire set of results was 0.305 ppm. The sample standard deviation was 0.042 ppm. The pooled standard deviation for the method was 0.002 ppm F^- from equation 6.4.

The quantity of fluoride in the samples was determined as a percentage as described above.

- **Sample 1**

The percentage of fluoride ions in each of the replicates was 0.010%, 0.010% and 0.010% respectively. The average quantity of fluoride for the set was 0.010 ± 0.000%F^- with RSD of 1%.

The percentage of fluoride contained in sample 2 and sample 3 was similarly determined and the results summarised in Table 7.35.

Table 7.35: % Fluoride for the normal calibration method for OM2SUL-GH4

Sample	% $[F^-]$	% $[F^-]_{ave}$
Sample 1	0.010; 0.010; 0.010	0.010 ± 0.000% F^-, RSD = 1.0%
Sample 2	0.013; 0.013; 0.013	0.013 ± 0.000% F^-, RSD = 0.8%
Sample 3	0.013; 0.013; 0.013	0.013 ± 0.000% F^-, RSD = 0.4%

The mean percentage fluoride for the entire set of results was 0.012%. The sample standard deviation was 0.002%.

The overall results have been summarized in Table 7.36.

Table 7.36.: Overall results for the analysis of the OM2SUL-GH4 sample.

Direct Ion Determination method	Normal Calibration method
% F^- = 0.012 ± 0.002	% F^- = 0.012 ± 0.002

7.8.3.7 Conclusion

The two methods of analysis which were used for this determination, namely, the direct ion measurement method and the normal calibration method, yielded the same results statistically as shown in Table 7.36. The amount of fluoride leached out by the sulphuric acid treatment of Omnia phosphogypsum was 72 % of the original amount. The amount of fluoride that is acceptable for the use of phosphogypsum as set retarder in the cement industry should not be more than 0.2% (Jarosiński, 1994). The total amount of fluoride obtained after the sulphuric acid treatment of Omnia phosphogypsum was 0.012%. Hence, the sulphuric acid purification method proved to be very efficient in the removal of fluoride from Omnia phosphogypsum.

7.9 The effect of treating phosphogypsum with water and lime

7.9.1 Introduction

Phosphogypsum has previously been treated with water and milk of lime in order to minimize the water soluble impurities (Ölmez and Erdem, 1989). A similar method was used by Van der Merwe (2001). In this section of the study, a second batch of Kynoch and Omnia phosphogypsums was obtained from the respective plants. Each phosphogypsum sample was treated with water and milk of lime and the extent of fluoride removal compared with untreated phosphogypsum. Since ion selective electrodes are pH dependent, the effect of pH of the sample solutions was also investigated in this work.

7.9.2 The effect of treating phosphogypsum with water and lime without pH control

In this work, the effect of washing two South African phosphogypsums, Omnia and Kynoch, with water or milk of lime was studied. Some of the samples were first washed with water and then fused at 900 °C, while a separate group of samples was initially washed with milk of lime followed by fusion at 900 °C. In this case, the pH of the sample solutions was not adjusted to a specific value prior to ISE measurements.

7.9.2.1 Sample preparation

- **Unwashed samples**

Kynoch batch 2 and Omnia batch 2 phosphogypsum samples were dried overnight at 45 °C. Each sample was cooled in a desiccator, ground with piston and mortar to fine particles, and mixed thoroughly. These represented the unwashed samples. A weighed portion of each sample was then fused as per method in Section 5.2.3.

- **Water washed samples**

A 12%(m/v) slurry of phosphogypsum (Omnia or Kynoch) was prepared in deionised water. The mixture was stirred on a magnetic stirrer for 10 minutes, filtered and the residue dried overnight at 45 °C. The dried sample was cooled in a desiccator and ground with piston and mortar to fine particles and mixed thoroughly. This represented the water-washed sample. A weighed portion of the sample was then fused as per method in Section 5.2.3.

- **Lime washed samples**

A 0.1 % (m/m) milk of lime solution was prepared by weighing 0.1g calcium hydroxide into a beaker and adding deionised water to give a 100g solution. The mixture was thoroughly mixed and then the undissolved calcium hydroxide left to settle. The supernatant liquid was used to wash the chemical gypsum samples. A 12%(m/v) slurry of phosphogypsum (Omnia or Kynoch) was prepared in the 0.1%(m/m) milk of lime solution. The mixture was stirred on a magnetic stirrer for 10 minutes, filtered and the residue dried overnight at 45 °C. The dried sample was cooled in a desiccator and ground with piston and mortar to fine particles and mixed thoroughly. This represented the lime-washed sample. A weighed portion of the sample was then fused as per method in Section 5.2.3.

Sampling data:

- **Unwashed Omnia**

An Omnia sample weighing 0.6256g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The sample solution was made up to 250 mL with deionised water.

- **Unwashed Kynoch**

A Kynoch sample weighing 0.6268g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The sample solution was made up to 250 mL with deionised water.

- **Water washed Omnia**

An Omnia sample weighing 0.6276g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The sample solution was made up to 250 mL with deionised water.

- **Water washed Kynoch**

A Kynoch sample weighing 0.6233g was mixed with 0.5 g ZnO and 2.5 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The sample solution was made up to 250 mL with deionised water.

- **Lime washed Omnia**

An Omnia sample weighing 1.2494g was mixed with 1.0 g ZnO and 5.0 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The sample solution was made up to 500 mL with deionised water.

- **Lime washed Kynoch**

A Kynoch sample weighing 1.2456g was mixed with 1.0 g ZnO and 5.0 g Na_2CO_3 in a platinum crucible and prepared as explained in the procedure described in Section 5.2.3. The sample solution was made up to 500 mL with deionised water.

7.9.2.2 Procedure for potential measurements

A measured volume (usually 10.00 mL) of the sample or standard was transferred into a 50 mL plastic beaker. An equal volume of TISAB was added to the sample or standard. A polyethylene coated magnetic stirrer bar was placed in the mixture, and the solution stirred by means of a magnetic stirrer. The fluoride indicator electrode and the reference electrode were immersed in the solution, and once the potential had stabilized, the measurement was taken. On the average, the potentials stabilized under five minutes.

7.9.2.3 Results

The direct ion concentration and the normal calibration procedures were applied for the analysis of Omnia and Kynoch phosphogypsums. The results for the direct ion concentration method are given in Table 7.37 (Omnia) and Table 7.38. (Kynoch). The results for the normal calibration method are given in Table 7.39 (fluoride standards) and Table 7.40 (Omnia and Kynoch samples).

Table 7.37: Results for the direct ion concentration mode for Omnia batch 2

Omnia sample	$[F^-]$ (ppm) for each replicate
Sample 1	0.801; 0.804; 0.799
Sample 2	0.593; 0.595; 0.595
Sample 3	1.05; 1.05; 1.05

Table 7.38: Results for the direct ion concentration mode for Kynoch batch 2

Kynoch sample	$[F^-]$ (ppm) for each replicate
Sample 1	4.80; 4.81; 4.81
Sample 2	5.38; 5.39;5.38
Sample 3	5,42; 5.44; 5.43

Table 7.39: Results for fluoride standards (normal calibration method)

Fluoride standard	[F$^-$] (ppm)	Potential (mV)
Standard 1	2.50 ppm	80.6
Standard 2	0.500 ppm	121.2
Standard 3	0.250 ppm	138.0
Standard 4	0.125 ppm	153.3
Standard 5	0.0500 ppm	177.0

Table 7.40: Results for the normal calibration method for both Omnia and Kynoch samples

Phosphogypsum samples	Potential (mV) for each replicate
Unwashed Omnia	127.3; 127.4; 127.5
Water washed Omnia	134.5; 134.3; 134.4
Lime washed Omnia	120.5; 120.6; 120.6
Unwashed Kynoch	81.6; 82.5; 81.7
Water washed Kynoch	78.6; 78.7; 78.7
Lime washed Kynoch	78.6; 78.6; 78.6

The percentage of fluoride in the samples was determined for the direct ion method as described previously. The results are summarised in Table 7.41 and Table 7.42.

Table 7.41: Results (% Fluoride) for Kynoch batch 2 (direct ion mode)

Kynoch batch 2 sample	% Fluoride	Mean % Fluoride
Unwashed	0.191 ; 0.192;0.192	Mean = 0.192 ± 0.001 RSD = 0.3%
Water washed	0.216;0.216;0.216	Mean = 0.216% ± 0.000 RSD = 0.1%.
Lime washed	0.218; 0.218;0.218	Mean = 0.218% ± 0.000 RSD = 0.2%

Table 7.42: Results (% Fluoride) for Omnia batch 2

Omnia batch 2 sample	% Fluoride	Mean % Fluoride
Unwashed	0.032; 0.032; 0.032	Mean = 0.032 ± 0.000 RSD = 0.6%.
Water washed	0.024; 0.024; 0.024	Mean = 0.024 ± 0.000 RSD = 0.2%.
Lime washed	0.042; 0.042; 0.042	Mean = 0.042 ± 0.000 RSD = 0.6%

Analysis of results by the normal calibration method for Omnia phosphogypsum:

All the raw data points were included in the derivation of the least squares, in line with the observation made from Figure 7.2 that the linear range should include the limits between 0.05 to 2.50 ppm F^-. Using the least square method (Section 6.2.6), the equation for the least squares line was

$$E = -56.38\log[F^-] + 103.47$$

where E is the potential (mV) measured and $[F^-]$ is the fluoride concentration (ppm). The standard deviation, s_r, about the regression was 0.88. The standard deviations about the slope, s_m, and of the intercept, s_b, were 0.68 and 0.54 respectively. The correlation coefficient was calculated using equation 6.16 and found to be 1.00.

The concentration of fluoride in each sample was then determined from the measured potentials and the dilution effects were accounted for as well. The results are given in Table 7.43

Table 7.43: Results for the normal calibration method of Omnia samples

Phosphogypsum samples	Fluoride concentration (ppm)
Unwashed Omnia	0.756; 0.753; 0.750
Water washed Omnia	0.563; 0.568; 0.566
Lime washed Omnia	0.998; 0.994; 0.994

The percentage of fluoride in each sample was determined as previously described and the results are summarised in Table 7.44.

Table 7.44: Results (% Fluoride) for Omnia batch 2 (normal calibration method)

Omnia batch 2 sample	% Fluoride	Mean % Fluoride
Unwashed	0.030 ; 0.030;0.030	Mean = 0.030 ± 0.000 RSD = 0.3%
Water washed	0.022;0.023;0.022	Mean = 0.022% ± 0.000 RSD = 4%.
Lime washed	0.040; 0.040;0.040	Mean = 0.040% ± 0.000 RSD = 0.1%

The concentration of fluoride in Kynoch phosphogypsum was determined in the same way as for Omnia phosphogypsum. The results are summarized in Table 7.45.

Table 7.45: Concentration of fluoride in various Kynoch samples – Normal calibration method

Phosphogypsum samples	Fluoride concentration (ppm)
Unwashed Omnia	4.885; 4.709; 4.866
Water washed Omnia	5.522; 5.500; 5.500
Lime washed Omnia	5.522; 5.522; 5.500

The quantity of fluoride in the samples was determined as for Omnia samples above and the results given in Table 7.46.

Table 7.46: Results (% Fluoride) for Kynoch batch 2 (normal calibration method)

Kynoch batch 2 sample	% Fluoride	Mean % Fluoride
Unwashed	0.195 ; 0.188;0.194	Mean = 0.192 ± 0.004 RSD = 2%
Water washed	0.222;0.221;0.221	Mean = 0.221% ± 0.001 RSD = 0.4%.
Lime washed	0.222;0.222;0.221	Mean = 0.222% ± 0.001 RSD = 0.4%

7.9.2.4 Discussion and conclusion

In the case of Kynoch phosphogypsum samples, subsequent pretreatments with water and lime yielded results which were higher than in the untreated phosphogypsum. The Omnia phosphogypsum results indicated removal of fluoride in the water treatment while the lime wash gave higher results. Hence, the amount of fluoride leached out with either water or lime was inconsistent for both Omnia and Kynoch phosphogypsums. The inconsistency of the results was attributed to the fact that the pH of the samples had not been adjusted to a uniform value prior to ISE measurements, as is recommended in the preparation of samples for analysis by this method. In highly acidic samples, the formation of HF and HF_2^- interferes with the detection of fluoride ions when using the ISE method, and high pH values render the electrode sluggish and falsely indicate high fluoride concentrations (Section 5.2.4).

7.9.3 Determination of the amount of fluoride in pH controlled phosphogypsum samples

7.9.3.1 Introduction

Since the amount of fluoride in the phosphogypsum samples (Omnia and Kynoch) has already been proved to be low, it was decided to use a spiking technique to enhance the analytical signal. The results obtained in Section 7.9.2, when the phosphogypsum samples were treated with water and lime without pH control, were inconsistent and did not indicate any trend in the effect of the pretreatment. For this part of the research, the pH of the samples was adjusted to a uniform value between pH 5 and 5.2. This was done to avoid the formation of HF and HF_2^- at pH values below 5. High pH values were avoided because the electrode tends to be sluggish and higher fluoride concentrations are falsely indicated.

7.9.3.2 Sample Preparation

An accurately weighed mass of the phosphogypsum (Kynoch batch 2 or Omnia batch 2) was mixed with weighed Na_2CO_3 and ZnO in a platinum crucible. The actual masses weighed were tabulated in Table 7.47. The sample mixture was then sintered for 30 minutes at 900 °C. The resulting melt was allowed to cool and then transferred to a 100 mL plastic beaker containing deionised water. A polythene coated magnetic stirrer bar was placed in the sample solution. While the solution was being stirred, the pH was adjusted to approximately pH 5 (See Table 7.47). The sample solution was then filtered using Whatman 41 filter paper and the filtrate transferred into a volumetric flask and made up to volume with deionised water.

Table 7.47: Phosphogypsum samples preparation information

Phosphogypsum Sample	Mass sample (g)	Mass ZnO (g)	Mass Na_2CO_3 (g)	Volumetric Flask (mL)	pH
Unwashed Kynoch	0.6250	0.5	2.5	250	5.1
Water washed Kynoch	0.6285	0.5	2.5	250	5.1
Lime washed Kynoch	0.6255	0.5	2.5	250	5.1
Unwashed Omnia	0.6273	0.5	2.5	250	5.1
Water washed Omnia	0.6292	0.5	2.5	250	5.1
Lime washed Omnia	0.6262	0.5	2.5	250	5.1

Sampling data:

- **Spiked Omnia samples**

An amount of 10.00 mL of a 10.00 ppm fluoride standard was pipetted into a 100 mL plastic beaker. 10.00 mL of the Omnia phosphogypsum sample was added to the standard followed by 20.00 mL of TISAB Buffer 1(as prepared in Section 5.2.4) solution to bring the total volume of the spiked sample to 40.00 mL. This made the concentration of added fluoride ion in the measuring vessel 2.50 ppm.

- **Spiked Kynoch samples**

10.00 mL of a 100.00 ppm fluoride standard was pipetted into a 100 mL plastic beaker. 10.00 mL of the Kynoch phosphogypsum sample was added to the standard followed by 20.00 mL of TISAB Buffer 1 solution to bring the total volume of the spiked sample to 40.00 mL. This made the concentration of added fluoride in the measuring vessel 25.0 ppm. Hence, the concentration of added fluoride in the Kynoch samples was ten times that of the Omnia samples. This decision was based on previous results which showed the percentage of fluoride in Kynoch phosphogypsum samples to be, on the average, in the region of ten times that of Omnia samples. Secondly, spiking the samples with the fluoride ion ensured that the Ion Meter measured at a higher fluoride concentration. This prevented working at fluoride ion concentrations that were too low and where calibration of the instrument might be irregular, as discussed previously.

- **Fluoride standards**

A series of four fluoride standards were prepared with fluoride ion concentrations of 5.00 ppm, 10.00 ppm, 50.00 ppm and 100.00 ppm respectively. Each of the prepared fluoride standard solutions was mixed with the same volume the TISAB Buffer 1solution for use during the calibration of the Ion Meter. Hence, on taking account of dilution effects, the concentrations of added fluoride ion in each of the fluoride standards were halved. This range of fluoride ion concentrations ensured that the Ion Meter was properly calibrated for the quantitative determination of fluoride in Omnia samples, as well as in the Kynoch samples.

7.9.3.3 Fluoride Analysis

The Metrohm Ion Meter was calibrated using the four standards mentioned above in the direct mode. The amount of fluoride in each sample was then determined and tabulated in Table 7.48.

Table 7.48: Fluoride ion concentration for both Kynoch batch 2 and Omnia batch 2 samples in the measuring vessel (Direct ion mode)

Phosphogypsum samples	[F$^-$] (ppm) for each replicate
Unwashed Kynoch	52.8; 52.9; 52.9
Water washed Kynoch	52.6; 52.7; 52.6
Lime washed Kynoch	51.9; 51.8; 51.8
Unwashed Omnia	5.81; 5.80; 5.82
Water washed Omnia	5.65; 5.64; 5.64
Lime washed Omnia	5.75; 5.74; 5.75

7.9.3.4 Calculations and analysis of results for Kynoch and Omnia phosphogysum samples

As described in Section 7.9.3.2, the Kynoch phosphogypsum samples were spiked with 10.00 mL of the 100.00 ppm standard, i.e. the added fluoride ion concentration was 25.00 ppm. However, the Ion Meter had a dilution correction of 2 programmed in the method of analysis. This implied that the fluoride ion concentration, after spiking, could be computed from the simplified equation

$$[F]_{total} = 2([F^-]_{spiking} + [F^-]_{present})$$

Where $[F^-]_{total}$ represented the observed concentration of fluoride from the Ion Meter reading, $[F^-]_{spiking}$ was the calculated concentration of fluoride introduced by spiking. The factor 2 was the dilution factor due to TISAB dilution effects, and $[F^-]_{present}$ represented the fluoride concentration of Kynoch phosphogypsum in the measuring vessel.

For example, the observed concentration of fluoride in the unwashed Kynoch phosphogypsum sample was 52.8 ppm for the first replicate (See Table 7.48), since the amount of fluoride added for spiking the samples was 25.0 ppm. The amount of fluoride ion present in the measuring vessel was

$$52.8 = 2(25.0 + [F^-]_{present})$$
$$\Rightarrow [F^-]_{present} = 1.4\ ppm$$

However, this calculation assumes a dilution factor of 2 for the sample (due to TISAB). The sample was, however, actually diluted four times i.e., 10.00 mL diluted to a final volume of 40.00 in the measuring vessel (see Section 7.9.3.2). The result has thus to be multiplied by a factor of 2 to give the final answer of 2.8 ppmF^- in the original Kynoch phosphogypsum sample. The amount of fluoride present in all analysed phosphogypsum samples was obtained in the same way. The results for both Omnia and Kynoch phosphogypsums are summarized in Table 7.49.

Table 7.49: Fluoride ion concentration for both Kynoch batch 2 and Omnia batch 2 samples in the original sample solutions

Phosphogypsum samples	$[F^-]$ (ppm) for each replicate
Unwashed Kynoch	2.80; 2.90; 2.90
Water washed Kynoch	2.60; 2.70; 2.60
Lime washed Kynoch	1.90; 1.80; 1.80
Unwashed Omnia	0.81; 0.80; 0.82
Water washed Omnia	0.65; 0.64; 0.64
Lime washed Omnia	0.75; 0.74; 0.75

The amount of fluoride for each of the Kynoch and Omnia phosphogypsums was determined as a percentage in each sample. In the case of the first replicate of the Kynoch phosphogypsum sample, the percentage of fluoride was computed as

$$[F^-] = 2.80\, ppm\ \textit{for first replicate}\ (\textit{Table}\ 7.29)$$

$$\%F^- = \frac{2.80\, mg/L \times 0.250 L \times 10^{-3} g/mg \times 100\%}{0.6250 g}$$

$$= 0.112\%$$

The percentage of fluoride in all other samples and their respective replicates was computed in a similar way. The results are tabulated in Table 7.50 (for Kynoch and Omnia phosphogypsum samples).

Table 7.50: Results (% Fluoride) for Kynoch batch 2and Omnia batch 2 – Direct ion measuring mode

Sample	% Fluoride
Unwashed Kynoch	0.112; 0.116; 0.116 Mean [F] = 0.115 ± 0.002; RSD = 2%
Water washed Kynoch	0.103; 0.107; 0.103 Mean [F] = 0.105 ± 0.002; RSD = 2%
Lime washed Kynoch	0.076; 0.072; 0.072 Mean [F] = 0.073 ± 0.002; RSD = 3%
Unwashed Omnia	0.032; 0.032; 0.033 Mean [F] = 0.032 ± 0.000; RSD = 1%
Water washed Omnia	0.026; 0.025; 0.025; Mean [F] = 0.025 ± 0.001; RSD = 4%
Lime washed Omnia	0.030; 0.030; 0.030 Mean [F] = 0.030 ± 0.000; RSD = 0.8%

7.9.3.5 Discussion and conclusion

The amount of soluble fluoride leached from Kynoch phosphogypsum by washing with water was 9%. On the other hand, washing Kynoch phosphogypsum with lime had the effect of removing 36% of soluble fluoride. This trend was somewhat reversed for the Omnia phosphogypsum in that water leached out 21% of the fluoride, while lime removed only 8%. It seems that Omnia phosphogypsum contains more soluble fluoride than Kynoch phosphogypsum. Hence, the effectiveness of the washing solvent on a given type of phosphogypsum depends on the amount of soluble fluoride in that solvent. Economic considerations and the purposes for which the phosphogypsum in question is required also play a role in the choice of solvent. Washing with water is more economical as water is readily available and, in most cases, relatively inexpensive.

7.10 Distribution of fluoride impurities in different particle size ranges of phosphogypsum

7.10.1 Introduction

Phosphogypsum has previously been purified by physical methods and then used in the building industry (Smadi et al., 1999). The authors washed the phosphogypsum with water using sieve no.100, and burnt it at various temperatures. In this work the particle size distribution of phosphogypsum was determined by sieving. The amount of fluoride impurities per particle size range of phosphogypsum was then determined by the Ion Selective Electrode method.

7.10.2 Sample preparation

- **Sieving**

A sample of Omnia batch 2 phosphogypsums was dried overnight at 45 °C. The sample was then allowed to cool in a desiccator. A 10g mass of the sample was sieved with sieves ranging in size from 75 µm to 1700 µm (Table 7.51). The fractions of the phosphogypsum collected on each sieve were placed in polythene sample bottles and stored in a desiccator. The samples of Kynoch batch 2 phosphogypsum were prepared in the same way (Table 7.52).

- **Fusion**

An accurately weighed mass of the phosphogypsum (Kynoch batch 2 or Omnia batch 2) of a particular particle size range (p) was mixed with weighed Na_2CO_3 and ZnO in a platinum crucible. The actual masses weighed are given in Table 7.51 for Omnia phosphogypsum and Table 7.52 for Kynoch phosphogypsum. The sample mixture was then sintered for 30 minutes at 900 °C. The resulting melt was allowed to cool and then transferred to a 100 mL plastic beaker containing deionised water. A polythene coated magnetic stirrer bar was placed in the sample solution. While the solution was being stirred, the pH was adjusted to approximately pH 5 (See Table 7.51). The sample solution was then filtered using Whatman 41 filter paper and the filtrate transferred into a volumetric flask and made up to volume with deionised water.

Table 7.51: Sampling data for Omnia batch 2 phosphogypsum

Omnia	Sieve size (p) (μm)	mass sample (g)	pH	Volume (mL)
SO.P	$p \leq 75$	0.6251	5.1	250
SO 75	$75 < p \leq 150$	1.2508	5.1	500
SO 150	$150 < p \leq 300$	0.6393	5.1	250
SO 300	$300 < p \leq 600$	0.2731	5.1	100

Table 7.52: Sampling data for Kynoch batch 2 phosphogypsum

Kynoch	Sieve size (p) (μm)	mass (g)	pH	Volume (mL)
SK.P	$p \leq 75$	1.2456	5.1	500
SK75	$75 < p \leq 150$	0.6273	5.1	250
SK 150	$150 < p \leq 300$	0.6232	5.2	250
SK 300	$300 < p \leq 600$	1.2502	5.1	500
SK 600	$600 < p \leq 1700$	0.6329	5.1	250
SK 1700	$p > 1700$	No Sample	-	-

7.10.3 Fluoride Analysis

20.00 mL of each sample solution was mixed with an equal volume of TISAB Buffer 1 solution and fluoride analysis was performed either by the direct ion concentration or by the normal calibration procedure, as explained in Section 7.5.

7.10.4 Results

The results for the direct ion concentration method are given in Table 7.53 (Omnia) and Table 7.54 (Kynoch). The results for the normal calibration method are given in Table 7.55 (fluoride standards), Table 7.56 (Omnia) and Table 7.57 (Kynoch).

Table 7.53: Results for the direct ion concentration method for Omnia batch 2 fractions

Omnia	Sieve size (μm)	[F⁻] (ppm)	Mean (ppm)
SO.P - replicates	$p \leq 75$	0.681; 0.681; 0.683	0.682±0.001 RSD =0.1%
SO 75 - replicates	$75 < p \leq 150$	0.464; 0.464; 0.463	0.464±0.001 RSD =0.2%
SO 150 - replicates	$150 < p \leq 300$	0.927; 0.925; 0.927	0.926±0.001 RSD =0.1%
SO 300	$300 < p \leq 600$	6.09; 6.10; 6.09	6.09±0.01 RSD =0.2%

Table 7.54: Results for the direct ion concentration method for Kynoch batch 2 fractions

Kynoch	Sieve size (μm)	[F⁻] (ppm)	Mean (ppm)
SK.P	$p \leq 75$	5.31; 5.32 and 5.29	5.31±0.02 RSD=0.3%
SK75	$75 < p \leq 150$	3.88; 3.90 and 3.91	3.90±0.02 RSD =0.4%
SK 150	$150 < p \leq 300$	4.68; 4.68 and 4.67	4.68±0.01 RSD =0.1%
SK 300	$300 < p \leq 600$	4.29; 4.31 and 4.30	4.30±0.01 RSD =0.2%
SK 600	$600 < p \leq 1700$	5.49; 5.49 and 5.48	5.49±0.01 RSD =0.1%
SK 1700	>1700	No Sample	

Table 7.55: Results for fluoride standards (normal calibration method)

Fluoride standard	[F$^-$] (ppm)	Potential (mV)
Standard 1	2.50 ppm	80.4
Standard 2	0.500 ppm	121.4
Standard 3	0.250 ppm	139.0
Standard 4	0.125 ppm	156.8
Standard 5	0.050 ppm	180.1

Table 7.56: Results for the normal calibration method for Omnia batch 2.

Omnia sample	Potential (mV) for each replicate
SO.P	131.2; 131.3; 131.4
SO75	142.4; 142.2; 142.3
SO150	123.2; 123.3; 123.4
SO300	75.6; 75.5; 75.6

Table 7.57: Results for the normal calibration method for Kynoch batch 2.

Omnia sample	Potential (mV) for each replicate
SK.P	78.6; 78.8; 78.8
SK75	86.7; 86.6; 86.9
SK150	82.0; 82.0; 81.9
SK300	84.3; 84.2; 84.3
SK600	78.1; 78.0; 78.1

7.10.5 Discussion of results for normal calibration method

The Ion Meter has to be calibrated on a routine basis as explained above in Section 7.8.2.4. Using the least square method, the equation for the least squares line derived from the data for standard solutions (Tables 7.55) was

$$E = 58.6923\log[F^-] + 103.7368$$

where E is the measured potential (mV) and $[F^-]$ is the fluoride concentration (ppm). The standard deviation, s_r, about the regression was 0.06. The standard deviations about the slope, s_m, and of the intercept, s_b, were 0.04 and 0.03 respectively. The correlation coefficient was calculated using equation 6.16 and found to be 1.00.

The concentration of fluoride in each sample was then determined from the measured potentials as follows:

- **Concentration of fluoride in Omnia fractions**

For SO.P 75 μm sample with a particle size range of $p \leq 75$, the average fluoride ion concentration was determined, as explained previously, to be 0.678 ±0.003 ppm F^-, with RSD of 0.4%.

Similarly, the average fluoride ion concentration for the SO75 sample with a particle size range of $75 < p \leq 150$, was 0.441 ±0.002 ppm F^-, with RSD of 0.4%.

The mean fluoride ion concentration for the SO150 sample with a particle size range of $150 < p \leq 300$ was 0.928 ±0.004 ppm F^-, with RSD of 0.4%.

The average fluoride ion concentration for the SO300 sample with a particle size range of $300 < p \leq 600$, was 6.04 ±0.02 ppm F^-, with RSD of 0.3%.

- **Concentration of fluoride in Kynoch fractions**

The amount of fluoride in Kynoch phosphogypsum samples was computed in the same way as for the Omnia phosphogypsum samples. The results were summarized in Table 7.58.

Table 7.58: Fluoride concentration in Kynoch batch 2 fractions
(Normal calibration method)

Kynoch samples	$[F^-]$ (ppm) for each replicate
SK.P	5.36; 5.32; 5.32
SK75	3.90; 3.92; 3.87
SK150	4.69; 4.69; 4.71
SK300	4.29; 4.30; 4.29
SK600	5.47; 5.49; 5.47

The percentages of fluoride in Omnia and Kynoch phosphogypsum samples were calculated as explained previously and the results, for the direct ion method, summarized in Table 7.59 and Table 7.60.

Table 7.59: Fluoride quantity (%) for Omnia batch 2 fractions

Omnia	Sieve size range (µm)	% F^- per replicate	Mean (%)
SO.P	$p \leq 75$	0.027; 0.027;0.027	0.027±0.000 RSD = 0.2%
SO 75	$75 < p \leq 150$	0.018; 0.018;0.018	0.018±0.000 RSD =0.1%
SO 150	$150 < p \leq 300$	0.036; 0.036; 0.036	0.036±0.000 RSD =0.1%
SO 300	$300 < p \leq 600$	0.223; 0.223; 0.223	0.223±0.000 RSD =0.1%

Table 7.60: Fluoride quantity (%) for Kynoch batch 2 fractions

Omnia	Sieve size range (µm)	% F^- per replicate	Mean (%)
SK.P	$p \leq 75$	0.213; 0.214; 0.212	0.213±0.001 RSD =0.5%
SK 75	$75 < p \leq 150$	0.155; 0.155; 0.156	0.155±0.001 RSD =0.4%
SK 150	$150 < p \leq 300$	0.188; 0.188; 0.187	0.188±0.001 RSD =0.4%
SK 300	$300 < p \leq 600$	0.172; 0.172; 0.172	0.172±0.000 RSD =0.2%
SK 600	$600 < p \leq 1700$	0.217; 0.217; 0.217	0.217 ±0.000 RSD =0.2%

The quantity of fluoride in Omnia and Kynoch samples derived from the normal calibration method was given in Table 7.61 and Table 7.62 respectively.

Table 7.61: % F^- for Omnia batch 2 fractions (Normal calibration method)

Omnia	Sieve size (µm)	% F^-	Mean (%)
SO.P	$p \leq 75$	0.0272;0.027;0.027	0.027±0.000 RSD =0.4%
SO 75	$75 < p \leq 150$	0.017; 0.018; 0.018	0.018±0.001 RSD =5%
SO 150	$150 < p \leq 300$	0.036; 0.036; 0.036	0.036±0.000 RSD =0.4%
SO 300	$300 < p \leq 600$	0.221; 0.222; 0.221	0.221±0.001 RSD =0.5%

Table 7.62: Fluoride quantity (%) for Kynoch batch 2 fractions (Normal calibration method)

Kynoch	Sieve size (µm)	% F^-	Mean (%)
SK.P	$p \leq 75$	0.213; 0.214; 0.212	0.213±0.001 RSD =0.5%
SK 75	$75 < p \leq 150$	0.155; 0.156; 0.154	0.155±0.001 RSD =0.6%
SK 150	$150 < p \leq 300$	0.188; 0.188; 0.189	0.188±0.001 RSD =0.5%
SK 300	$300 < p \leq 600$	0.172; 0.172; 0.172	0.172 ±0.000 RSD =0.1%
SK 600	$600 < p \leq 1700$	0.216; 0.217; 0.216	0.216 ±0.001 RSD =0.5%

7.10.6 Conclusion

The quantity of fluoride in various fractions of Omnia batch 2 phosphogypsum samples, obtained through the use of the direct ion measurement method and the normal calibration method, is consistent as indicated in Tables 7.59 and 7.61. The direct ion concentration method also corroborated the results obtained for the fractions of the Kynoch phosphogypsum samples by the use of the normal calibration method, as shown in Table 7.60 and Table 7.62. The average results for Omnia phosphogypsum indicate that F^- is concentrated in "lumps" with larger particle size compared to the finer particles. The higher particle size range of $300\mu m < p \leq 600\mu m$ in Omnia phosphogypsum contains as much as ten times the amount of fluoride contained in lower particle size ranges of $150\mu m < p \leq 300\mu m$ and $p \leq 75\mu m$. However, these "lumps" with a particle size range of $300\mu m < p \leq 600\mu m$ in Omnia constitute only 14.2% of the phosphogypsum (Table 4.1). On the other hand, the amount of fluoride contained in each of the particle size ranges of Kynoch phosphogypsum (batch 2) investigated above (Table 7.40 and Table 7.42) is approximately 0.2%. The particle size for all subsequent determinations was fixed by sieving all phosphogypsum samples with a sieve with a pore size of 150μm.

The direct ion measurement method is faster and lends itself to ease of automation because it reads the concentration of the analyte directly in any specified concentration unit. The normal calibration method, on the other hand, is relatively slow as it requires many calibration standards. The normal calibration method also requires the construction of calibration curves, which adds to the slowness of the technique. The direct ion method is more expensive in that it requires a special potentiometer which can read concentrations directly. The normal calibration method can be performed with a simple, inexpensive potentiometer. However, both methods give the same level of precision as can be seen in Tables 7.9, 7.18, 7.27 and 7.36. In general, the fluoride ion selective electrodes are not specific but merely selective towards the fluoride ion. They respond to hydrogen ions and are, therefore, pH-limited. Their response is fairly rapid as explained in Section 7.4. However, at very low fluoride concentrations, the electrode response becomes fairly sluggish (as shown in Figures 7.1 to 7.4.) resulting in a non-linear response.

Chapter 8 Ion Chromatography method-Experimental

8.1 Introduction

Ion chromatography has proved to be a very versatile analytical tool with a wide application in fields as diverse as water analysis, the semiconductor industry, medicine, agriculture, mining and metal purification and environmental protection. In this study, ion chromatography was applied in the qualitative and quantitative determination of fluoride in South African chemical gypsum (phosphogypsum and titangypsum). All samples analysed by the ion chromatographic method were also subjected to the ISE analysis (see Chapter 7) for comparison.

8.2 Instrumentation

A Dionex 4000i HPLC system with a conductivity detector was used. The system has been described in detail in Section 2.2.2.4.

8.3 Chemicals and Reagents

- A carbonate-bicarbonate stock solution mixture was prepared with concentrations of 280 mM $NaHCO_3$ and 230mM Na_2CO_3. This was diluted as required to serve as the eluent in specified experiments.

- An eluent concentrate stock solution was purchased from Dionex. Diluting the concentrate ten times yielded 1.0 mM $NaHCO_3$ and 3.5 mM Na_2CO_3.

This was used as eluent in specified experiments.

- A 0.025 M sulphuric acid solution was used as a suppressor regenerant solution.

- A 1000 ppm chloride stock solution was prepared from KCl and diluted to serve as chloride standards as required in certain experiments.

- A 1000 ppm nitrate stock solution was prepared from $NaNO_3$ and diluted to serve as nitrate standards as required in certain experiments.

- A 1000 ppm nitrite stock solution was prepared from $NaNO_2$ and diluted to serve as nitrite standards as required in certain experiments.

- A 1000 ppm sulphate stock solution was prepared from Na_2SO_4 and diluted to serve as sulphate standards as required in certain experiments.

- A 1000 ppm phosphate stock solution was prepared from Na_2HPO_4 and diluted to serve as phosphate standards as required in certain experiments.

- Various fluoride standard solutions were prepared by serial dilution of the stock solution prepared, as explained in Section 7.3.

The eluents and other stock solutions mentioned above were used throughout the study for a variety of purposes. For example, a stronger eluent composition was used to flush the separator, a certain standard was used to check whether the system was operating consistently, various standards were used for determination of retention times of the various ionic species, etc. The actual concentrations of the reagents used in specific cases were stated in each case.

8.4 Samples

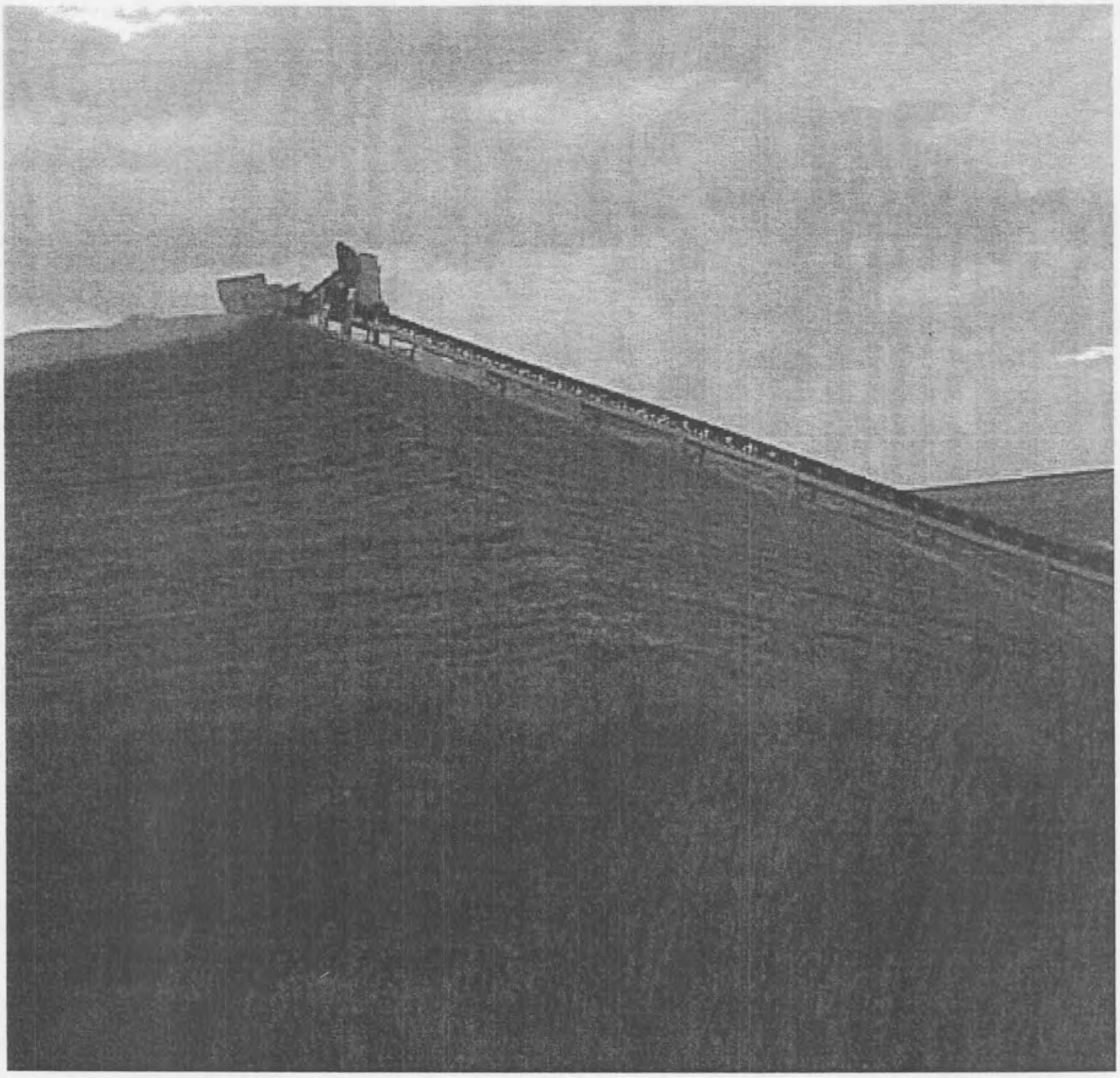
The samples were sourced from Kynoch phosphate fertilizer plant and Tioxide titanium dioxide plant. The Kynoch phosphogypsum was labelled batch 3 and the Tioxide titangypsum was labelled batch 1. At this stage Omnia phosphogypsum samples were not collected from the plant because the emphasis of the work was to develop the chromatographic method and test it against the ion selective electrode method. Hence, the two chemical gypsums, Kynoch phosphogypsum and Tioxide titangypsum samples, were considered sufficient.

8.4.1 Kynoch phosphogypsum samples

Three samples were taken at the Kynoch fertilizer plant situated in Potchefstroom in the NorthWest Province. The first sample was a crushed phosphate rock. This sample was labelled Phosphate Rock Sample Unwashed (PRSU). Secondly, a sample of phosphogypsum was taken directly from the phosphoric acid filtration pans (after washing with water). This sample was labelled Filter Pan Sample Unwashed (FPSU). The third sample was collected from the phosphogypsum stockpile and labelled Slime Dam Sample Unwashed (SDSU).The letter 'U' in the labelling implies that the sample is to be analysed **u**nwashed in the laboratory.

The stockpile dump is situated approximately three kilometres from the phosphoric acid plant. The phosphogypsum slurry is sluiced out to this repository, together with the process water. The process water is then circulated for re-use at the plant. A picture of the Kynoch phosphogypsum stack is shown in Figure 8.1.

Figure 8.1: Kynoch phosphogypsum stack



8.4.2 Tioxide titangypsum samples

A portion of the chemical gypsum produced at the Tioxide plant in Durban, KwaZulu-Natal province, was sampled directly from the filtration unit. This sample was labelled Tioxide Chemical Gypsum (TCGU).

8.4.3 Sample Preparation

8.4.3.1 Particle size reduction – Sieving process

A portion of the chemical gypsum sample (phosphogypsum or titangypsum) was crushed to fine particles with a mortar and piston. It was then placed in an oven to dry overnight at 45 °C. The sample was allowed to cool in a desiccator. It was then transferred to a 150µm aperture sieve (Analysette 3 Spartan pulverisette 0 – Fritsch instrument). It was sieved for a period of 30 minutes. The sieved sample was then stored in a plastic sample container and placed in a desiccator.

8.4.3.2 Sample fusion and dissolution

An accurately weighed mass of the phosphogypsum or titangypsum was mixed with weighed Na_2CO_3 and ZnO in a platinum crucible. The actual masses weighed are tabulated in Table 8.1 (Kynoch batch 3 samples) and Table 8.2 (Tioxide batch 1 samples). The mixtures were then sintered for 30 minutes at 900 °C. The resulting melt was allowed to cool and then transferred to a 100 mL plastic beaker containing deionised water. A polythene coated magnetic stirrer bar was placed in the sample solution. While the solution was being stirred, the pH was adjusted to approximately 5. The sample solution was then filtered using Whatman 41 filter paper. The filtrate was transferred into a volumetric flask and made up to volume. Details of each sample data are given in Table 8.1 and 8.2.

8.4.3.3 Sample purification

The lime and water washed samples were prepared as explained in Section 4.3. The lime washed samples and the water washed samples were fused and dissolved as explained above. The purified samples are denoted with an extension on the sample name to indicate the washing reagent used. 'W' indicates the sample has been water washed, 'L' denotes lime washing while 'U' denotes an unwashed sample. For example, FPSU, FPSW and FPSL would indicate unwashed, water washed and lime washed Kynoch phosphogypsum samples which were collected from the filtration pans as explained previously in Section 8.4.1.

The sample preparation data for each sample are given in Table 8.1 and 8.2.

Table 8.1: Kynoch batch 3 samples preparation information

Sample	Mass sample (g)	Mass ZnO (g)	Mass Na_2CO_3 (g)	Volumetric Flask (mL)	pH
PRSU	0.6254	0.5	2.5	250	5.1
FPSU	0.6248	0.5	2.5	250	5.2
SDSU	0.6254	0.5	2.5	250	5.1
FPSW	0.6283	0.5	2.5	250	5.2
SDSW	0.6247	0.5	2.5	250	5.2
FPSL	0.6260	0.5	2.5	250	5.2
SDSL	0.6256	0.5	2.5	250	5.2

Table 8.2: Titangypsum batch 1 samples preparation information

Sample	Mass sample (g)	Mass ZnO (g)	Mass Na_2CO_3 (g)	Volumetric Flask (mL)	pH
TCGU	0.6255	0.5	2.5	250	5.1
TCGW	0.6256	0.5	2.5	250	5.2
TCGL	0.6249	0.5	2.5	250	5.1

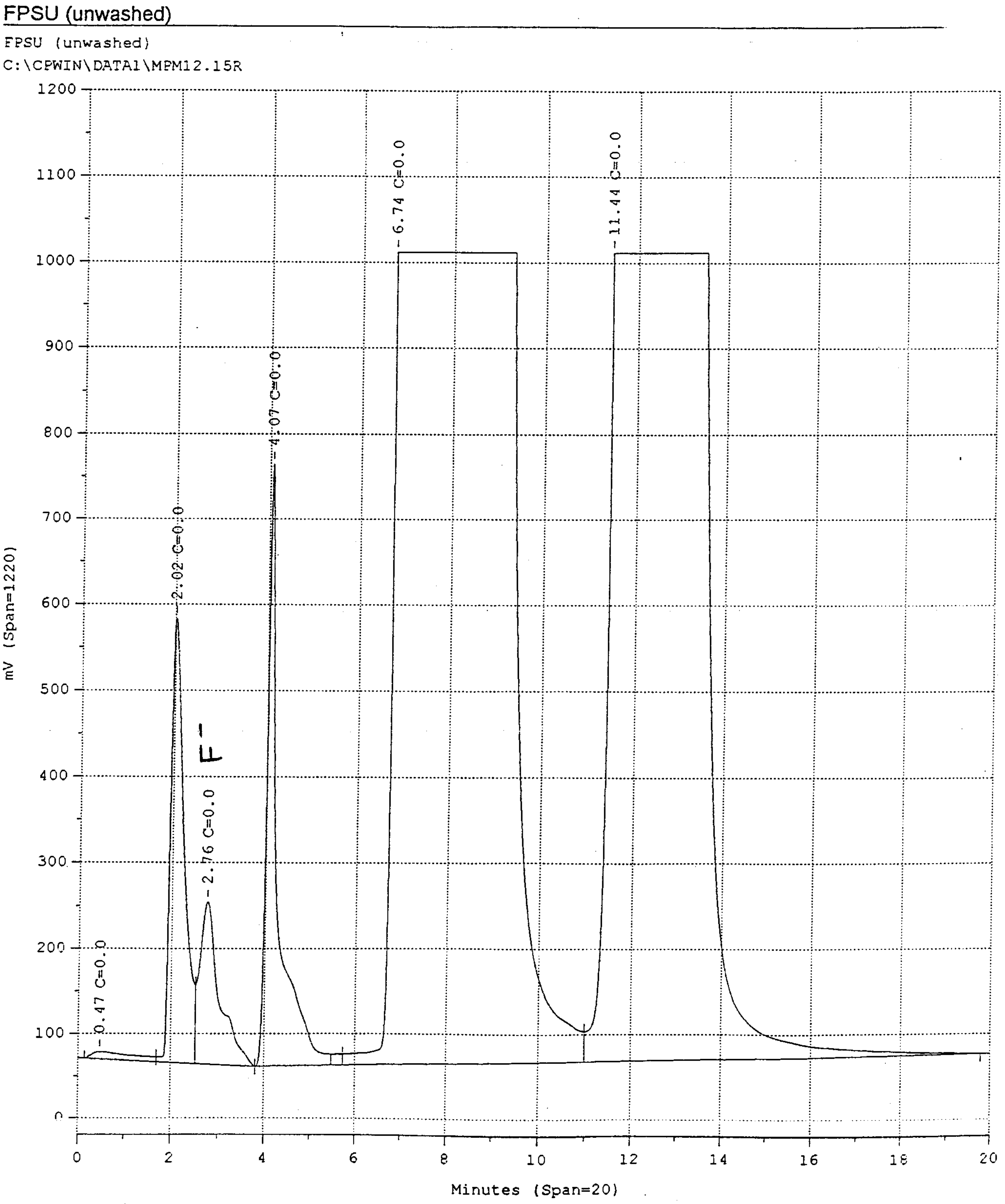
8.5 Column Overloading

8.5.1 Introduction

The phosphogypsum and titangypsum samples are very complex and contain various impurity ions such as sulphates, chlorides, phosphates and fluorides, among others. Although the focus of this study is on the fluoride ion impurity, other ions present in the sample have an influence on the column condition.

The average elution time of all ionic species detected in the Kynoch phosphogypsum samples was 18 minutes (see chromatogram given in Figure 8.2), when the eluent strength was 3.5 mM carbonate and 1.0 mM bicarbonate. However, changing the eluent strength to a more dilute composition of 40:60 eluent to water (mixture which is 3.5 mM carbonate and 1.0 mM bicarbonate, diluted 40:60 with deionised water) while keeping other parameters constant, increased the average elution time to 35 minutes (see chromatogram given in Figure 8.3). Hence, the column becomes susceptible to overloading when the analyst switches from one eluent strength to another without effectively conditioning the column; a similar result occurs when the complex ions become progressively retained.

Figure 8.2: Chromatogram of FPSU sample with undiluted eluent

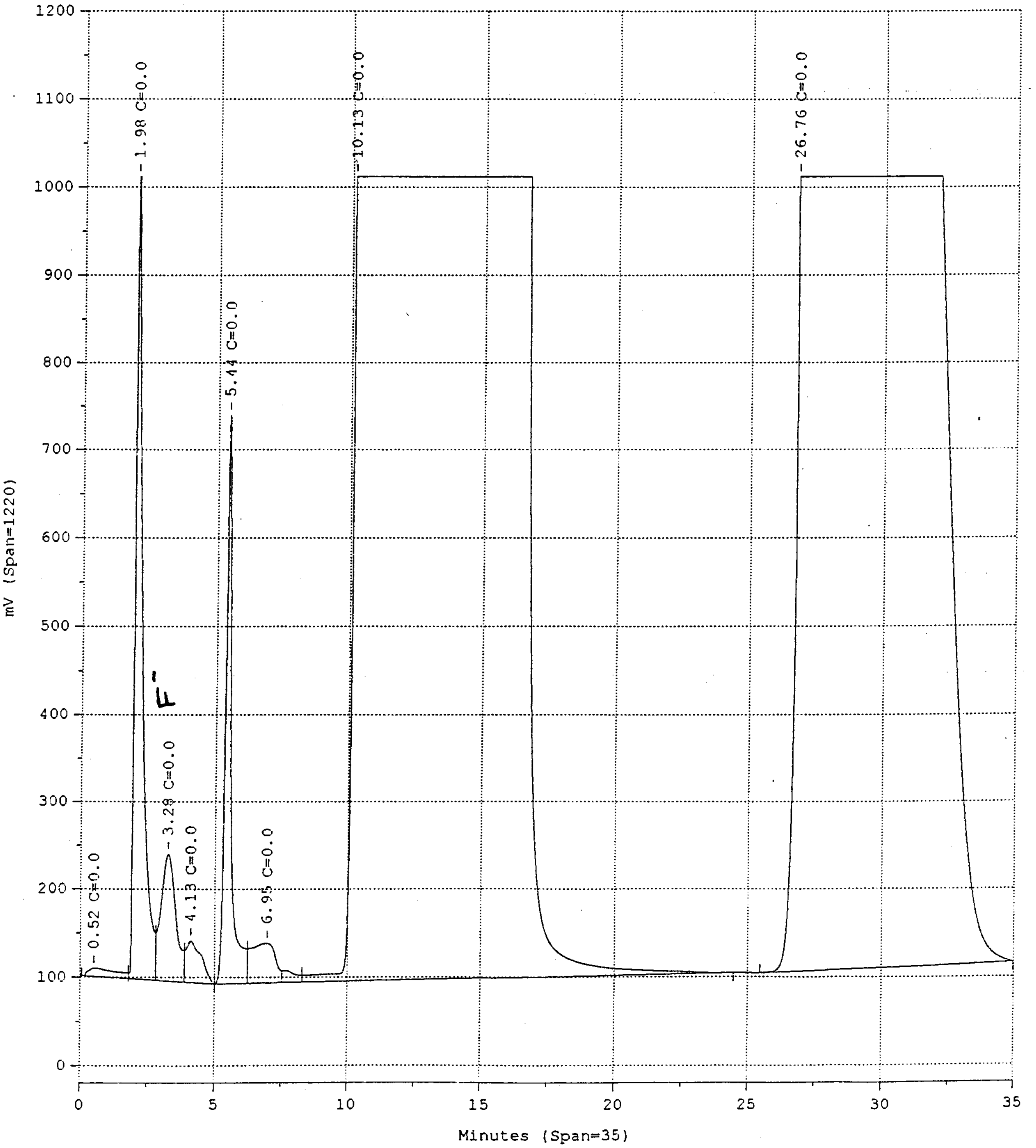


Sample Name: **FPSU (unwashed)**

Figure 8.3: Chromatogram of FPSU sample with diluted eluent such that eluent:water is 40:60

FPSU (unwashed)

FPSU (unwashed)
C:\CPWIN\DATA1\MPM12.16R



Sample Name: **FPSU (unwashed)**

8.5.2 Experimental

8.5.2.1 Sample

The Kynoch filter pan phosphogypsum sample (FPSU), prepared as described in Section 8.4, was used. Some of the samples were spiked with added fluoride ion to ensure the identification of the correct peak (fluoride retention time) on the chromatograms.

8.5.2.2 Fluoride Analysis

The FPSU samples were chromatographed over 16 consecutive injections and the retention time of the fluoride ion was recorded in each case. The chromatographic conditions were an eluent mixture which was 3.5 mM carbonate and 1.0 mM bicarbonate, and a flow rate of 1.2 mL/minute. The sample size was fixed in each case at 50 microlitres.

8.5.3 Results

The chromatograms were printed for the time span of six minutes only since the fluoride peak emerged within four minutes under the specified chromatographic conditions. A summary of the results is provided in Table 8.3. The typical chromatograms are shown in chromatograms given in Figure 8.4, Figure 8.5 and Figure 8.6.

Table 8.3: Investigation of retention time as a function of number of injections for FPSU sample

Retention time (minutes)	Number of injections
3.01	1
2.99	2
2.98	3
3.03	4
2.99	5
2.98	6
2.99	7
2.99	8
2.98	9
2.99	10
2.99	11
3.00	12
3.00	13
2.98	14
2.99	15
3.04	16

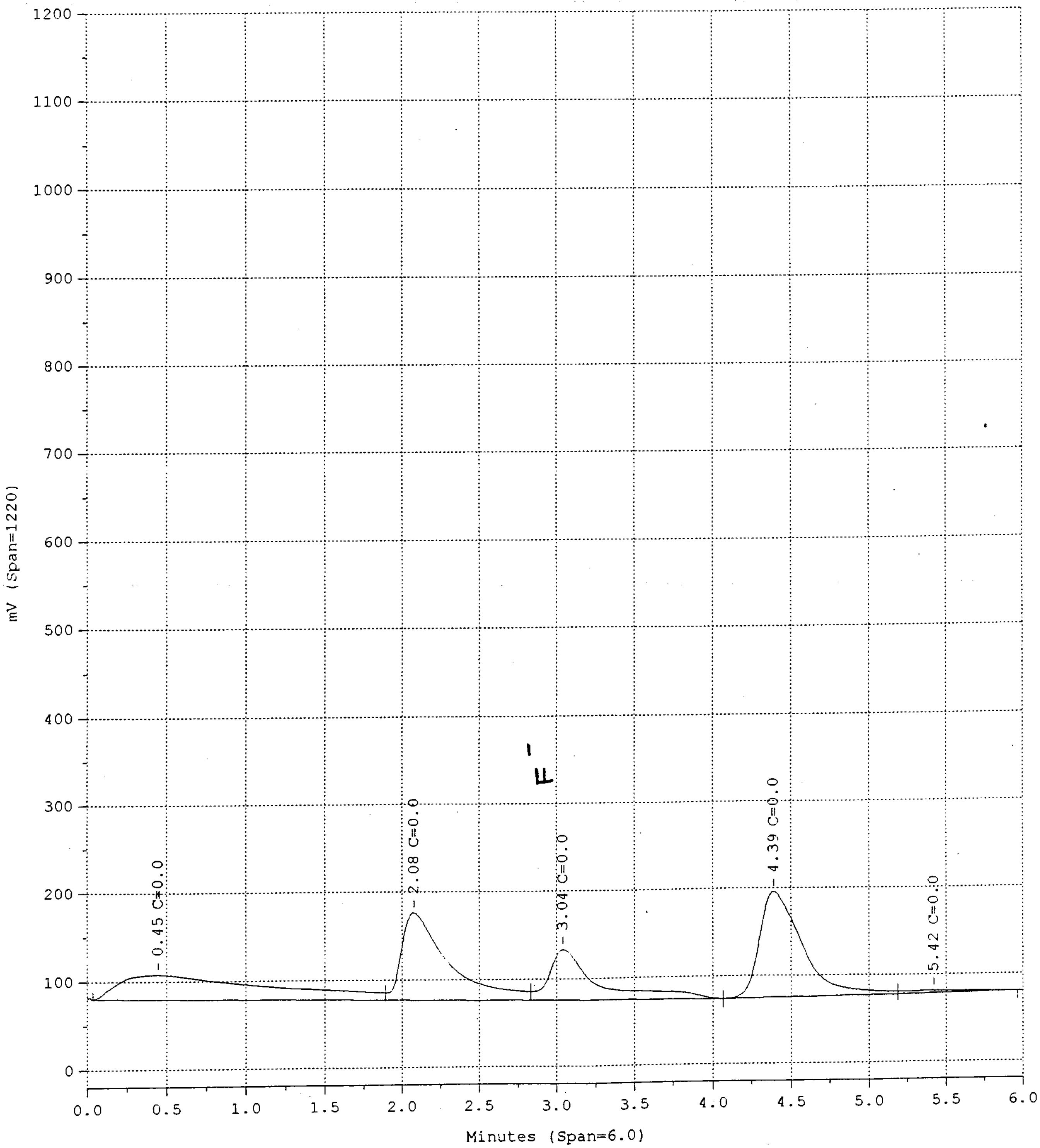
8.5.4 Conclusion

The results given in Table 8.3 yielded a mean retention time of 3.00 ±0.02 minutes with RSD of 0.7%. These results indicate that the retention time remained unchanged at fixed chromatographic conditions. The analytical column was therefore not overloaded, and also no carryover was implicated as the number of injections increased. The data are plotted in Figure 8.7.

Figure 8.4: Chromatogram of FPSU sample without added fluoride

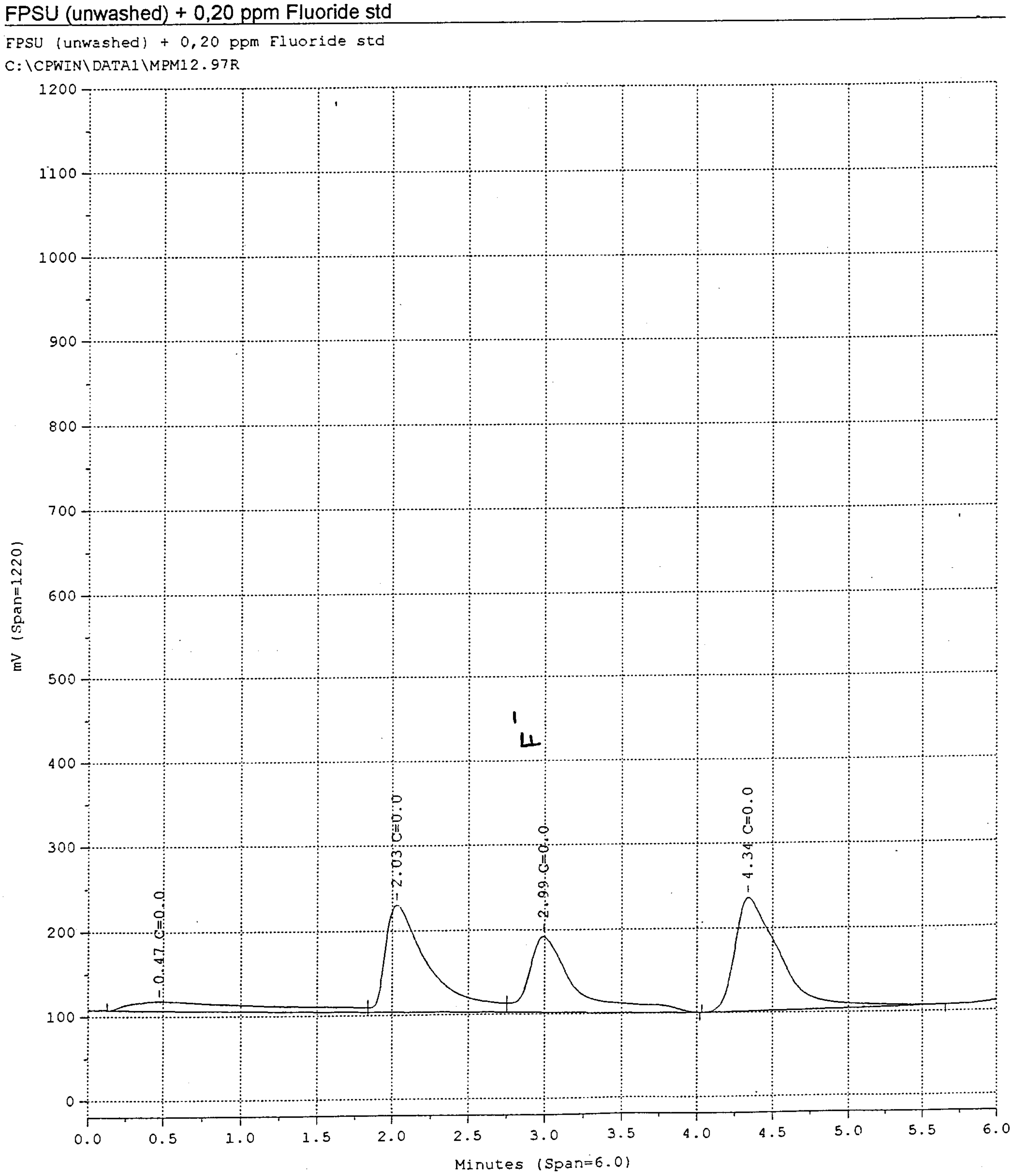
FPSU (unwashed)

FPSU (unwashed)
C:\CPWIN\DATA1\MPM13.13R



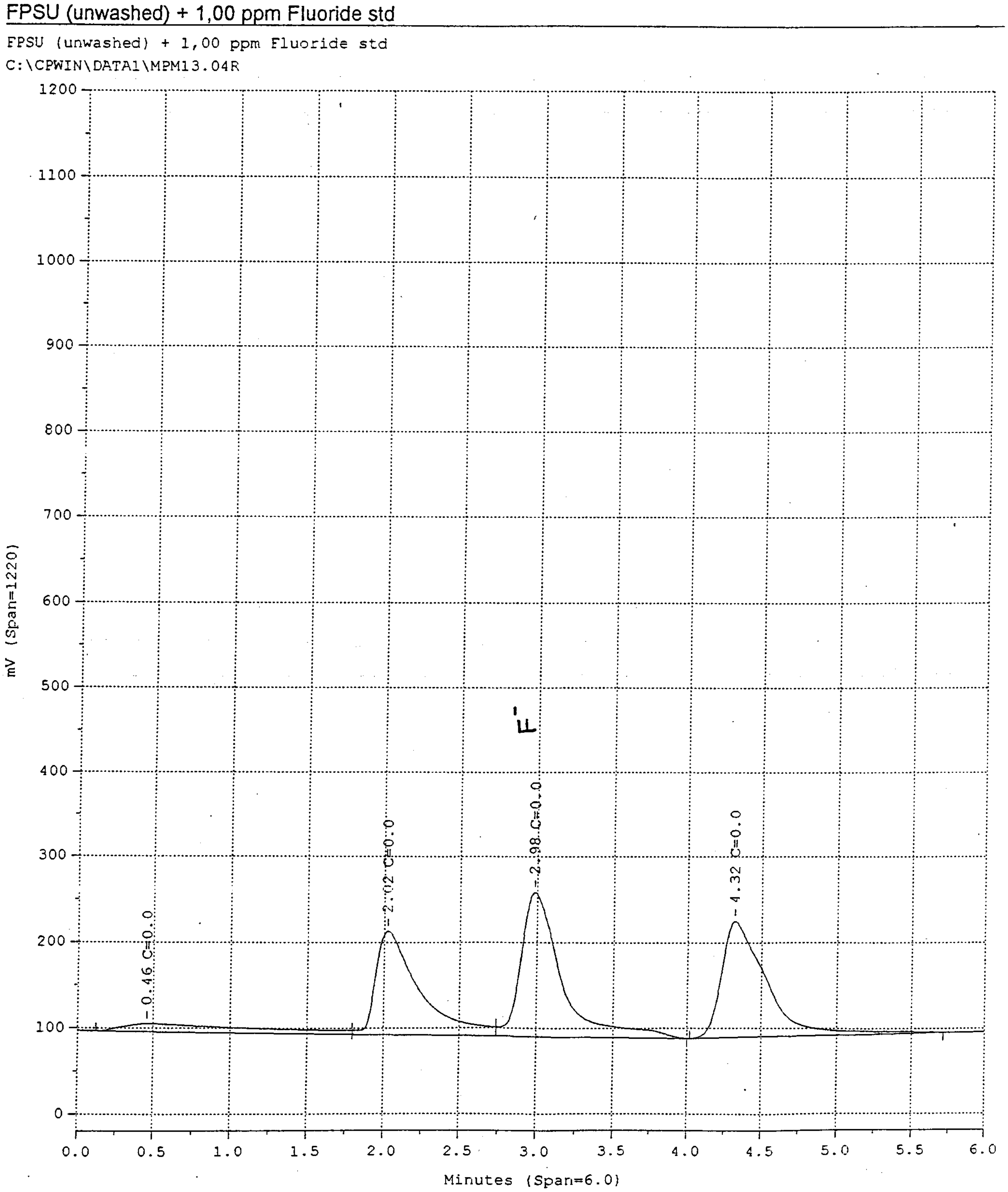
Sample Name: **FPSU (unwashed)**

Figure 8.5: Chromatogram of FPSU sample with added fluoride (0.20 ppm F$^-$)



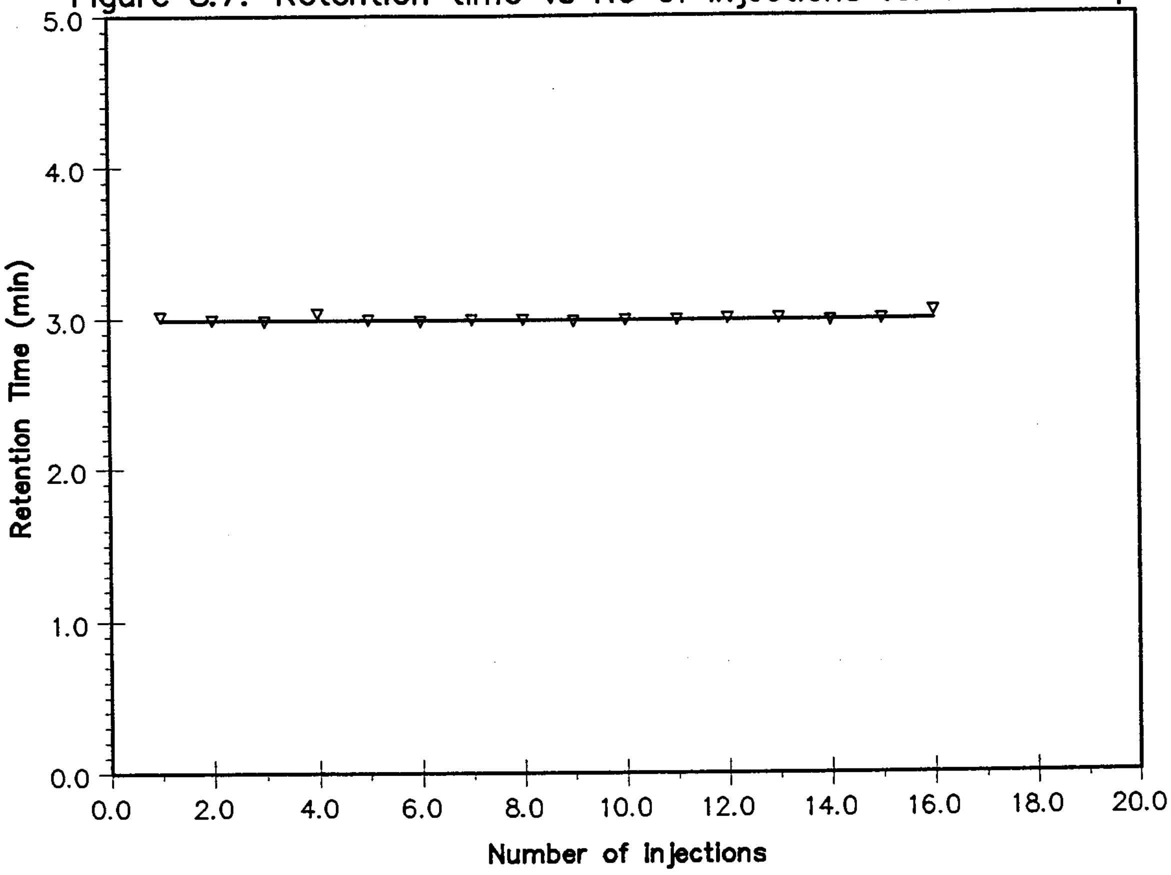
Sample Name: **FPSU (unwashed) + 0,20 ppm Fluoride std**

Figure 8.6: Chromatogram of FPSU sample with added fluoride (1.00 ppm F^-)



Sample Name: **FPSU (unwashed) + 1,00 ppm Fluoride std**

Figure 8.7: Retention time vs No of injections for FPSU sample



8.6 Investigation of the species that coelute close to the fluoride peak

8.6.1 Introduction

It has been shown that under similar operating conditions as those described below in Section 8.6.2 (Dionex AS1 to AS4 stationary phase, carbonate-bicarbonate eluent, etc.), fluoride and formate ion elute very close to the void volume (Weiss, 1986). In this study, an investigation was carried out to determine whether formate and acetate ions interfere with the determination of the fluoride ion. This was done by determining the retention time of the species as a function of eluent strength and comparing it to that of the fluoride ion.

8.6.2 Chromatographic conditions

The eluent was prepared as a mixture of 3.5 mM CO_3^{2-} and 1.0 mM HCO_3^-. This was referred to as 100% eluent. Several dilutions of this eluent with deionised water (Table 8.4) were prepared and used in subsequent determinations. The flow rate was maintained at 1.2 mL/minute. The sample size was fixed in each case at 50 microlitres. The separator used was the AS14 column and AG14 guard. The membrane suppressor was regenerated with a 0.0250M H_2SO_4 solution.

The instrumentation used was the Dionex 4000i HPIC with a conductivity detector.

8.6.3 Reagents

- A seven anion standard (Dionex) containing 5.00 ppm F^-, 7.50 ppm Cl^-, 25.0 ppm NO_2^-, 25.0 ppm Br^-, 25.00 ppm NO_3^-, 37.5 ppm $H_2PO_4^-$ and 37.5 ppm SO_4^{2-}.

- 5.00 ppm formate (potassium formate, Fluka AG) ion solution.
- 10.00 ppm acetate (anhydrous sodium acetate) ion solution.
- A three component mixture that contained 5.00 ppm fluoride, 10.00 ppm acetate ion and 10.00 ppm formate ion.

8.6.4 Procedure

The strength of the eluent was changed from the initial concentration of 3.5 mM CO_3^{2-} / 1.0 mM H CO_3^- (referred to as 100% eluent) to more dilute concentrations as shown in Table 8.4. The three component mixture of fluoride, acetate and formate ions was chromatographed for each of the eluent strengths under study. The seven anion standard was chromatographed for only the 100% eluent and the 50:50 (eluent: water) strengths just to provide an impression of where each of the ions would occur if they formed part of the impurities in the samples. Since these ions were not coeluting with the fluoride ion, it was not deemed necessary to chromatograph them at all eluent strengths studied.

8.6.5 Results

An example of the chromatograms obtained is given for the seven anion standard in chromatogram shown in Figure 8.8. A summary of retention times as a function of eluent strength for various anions is given in Table 8.4. The chromatograms of the mixture of fluoride, acetate and formate ions, as a function of eluent strength are given in Figures 8.9 to 8.13.

Figure 8.8: Chromatogram of Dionex's seven anion standard mixture

4xDil Dionex 7anion stds

4xDil Dionex 7anion stds
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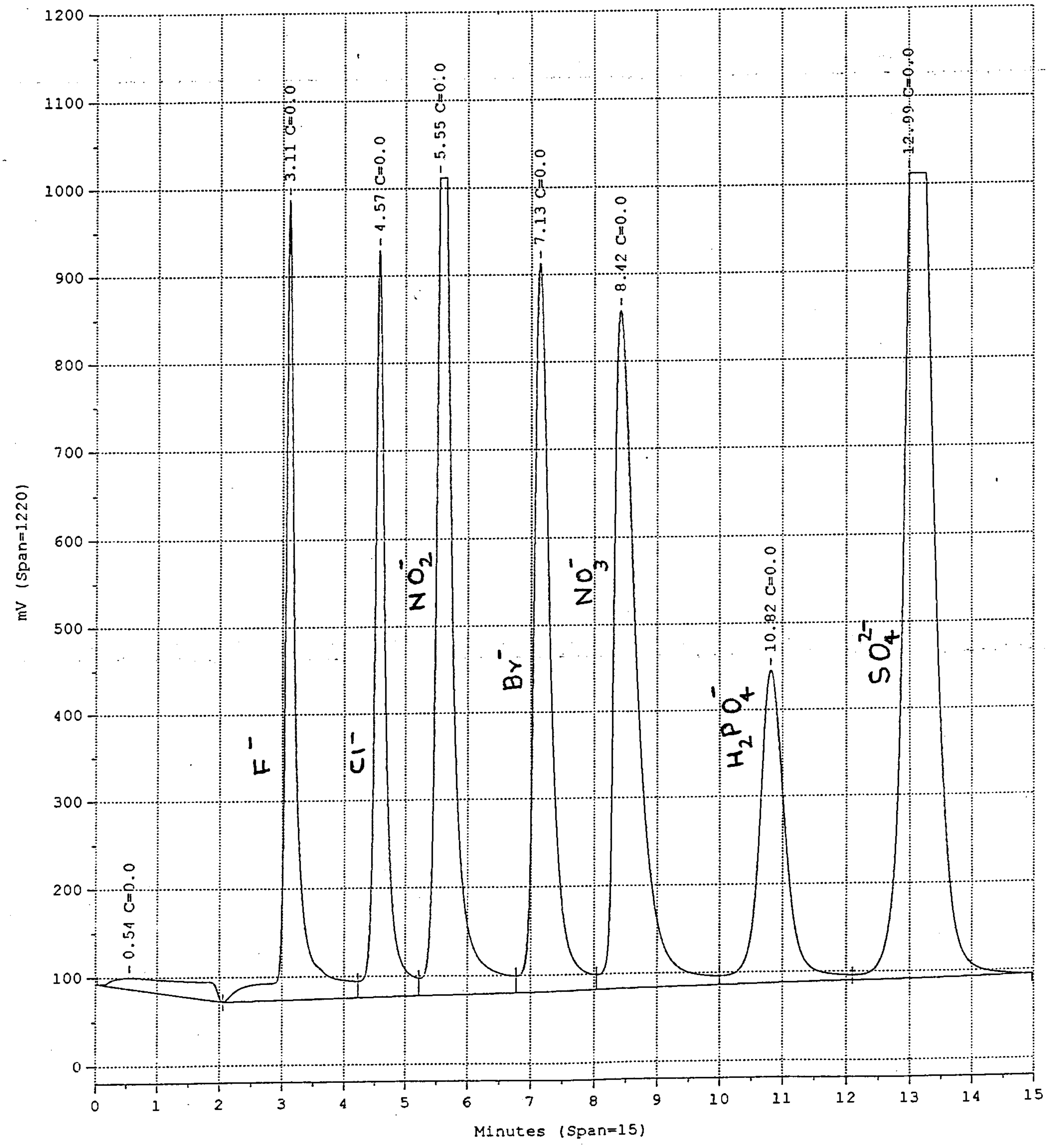


Sample Name: **4xDil Dionex 7anion stds**

Table 8.4: Retention times as a function of eluent concentrations for various anions

Retention Time (minutes)									
Eluent: H_2O	$CH_3CO_2^-$	HCO^-	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	$H_2PO_4^-$	SO_4^{2-}
100:0	3.50	3.65	3.13	4.57	5.55	7.13	8.42	10.82	12.99
70:30	PR	4.02	3.40	-	-	-	-	-	-
60:40	4.06	4.31	3.57	-	-	-	-	-	-
50:50	4.29	4.50	3.78	5.79	7.22	9.24	10.96	21.11	25.76
40:60	PR	4.55	3.79	-	-	-	-	-	-
30:70	PR	5.34	4.40	-	-	-	-	-	-
20:80	5.75	6.06	4.97	-	-	-	-	-	-

Note: PR refers to poor resolution.

8.6.6 Discussion and conclusion

As expected from theory, the retention time generally increases with dilution of the eluent. The fluoride peak resolution from the acetate and formate doublet is clearly enhanced with the dilution of the eluent, as shown in Figures 8.9 to 8.13. The acetate-formate doublet was very difficult to resolve even with the eluent concentration range used. The eluent concentration of 20:80 (eluent:water) managed effectively to separate the peaks albeit with a massive compromise of sensitivity, as shown in Figure 8.12. Clearly, the acetate and formate ions do not interfere with the resolution of the fluoride peak as both their peaks are eluted approximately 0.5 minutes further than the fluoride peak for all the eluent strengths investigated.

Figure 8.9: Chromatogram of a mixture whose composition is 5.00 ppm F^-,10.00 ppm formate and 20.00 ppm acetate (eluent:water = 60:40)

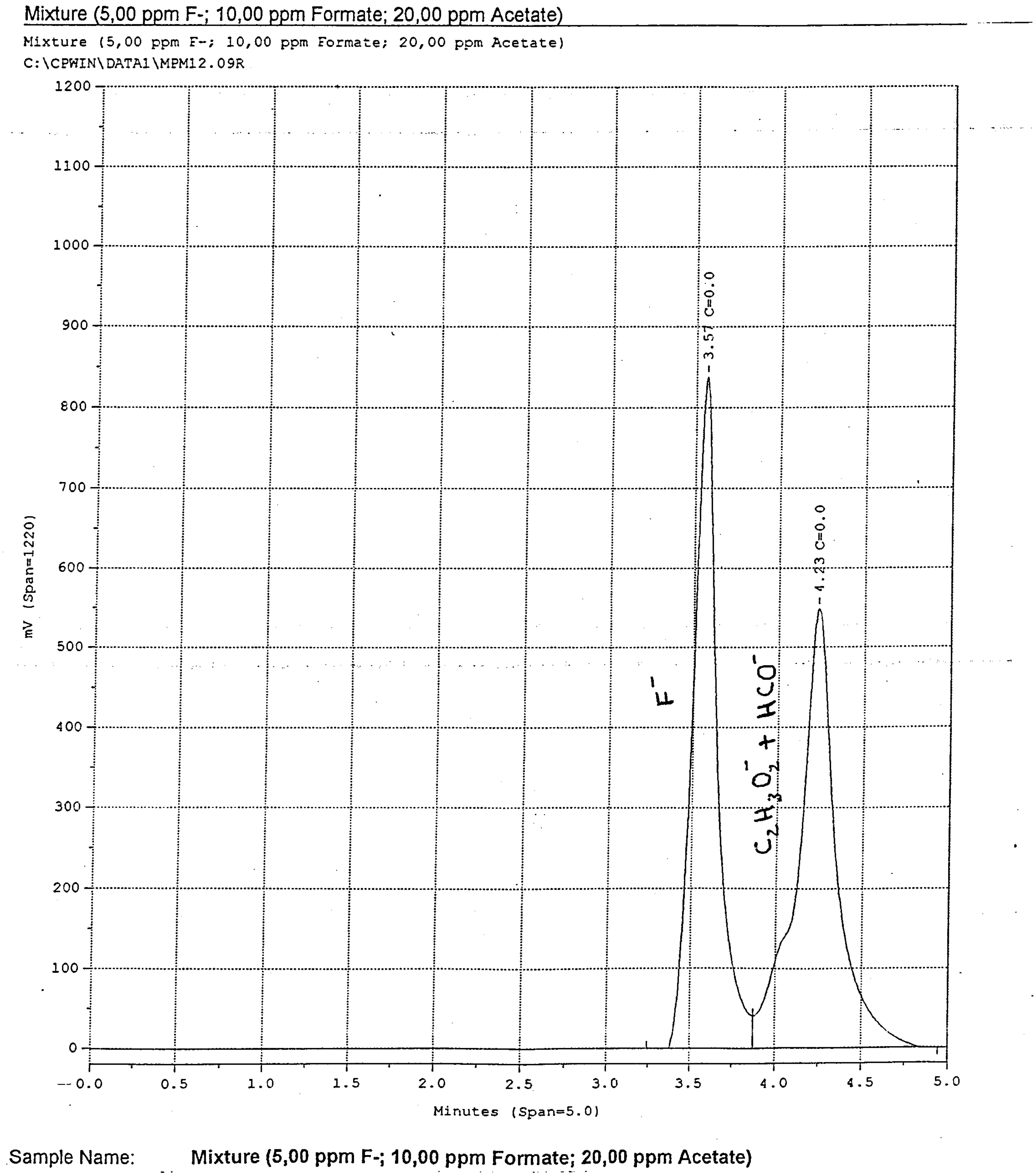
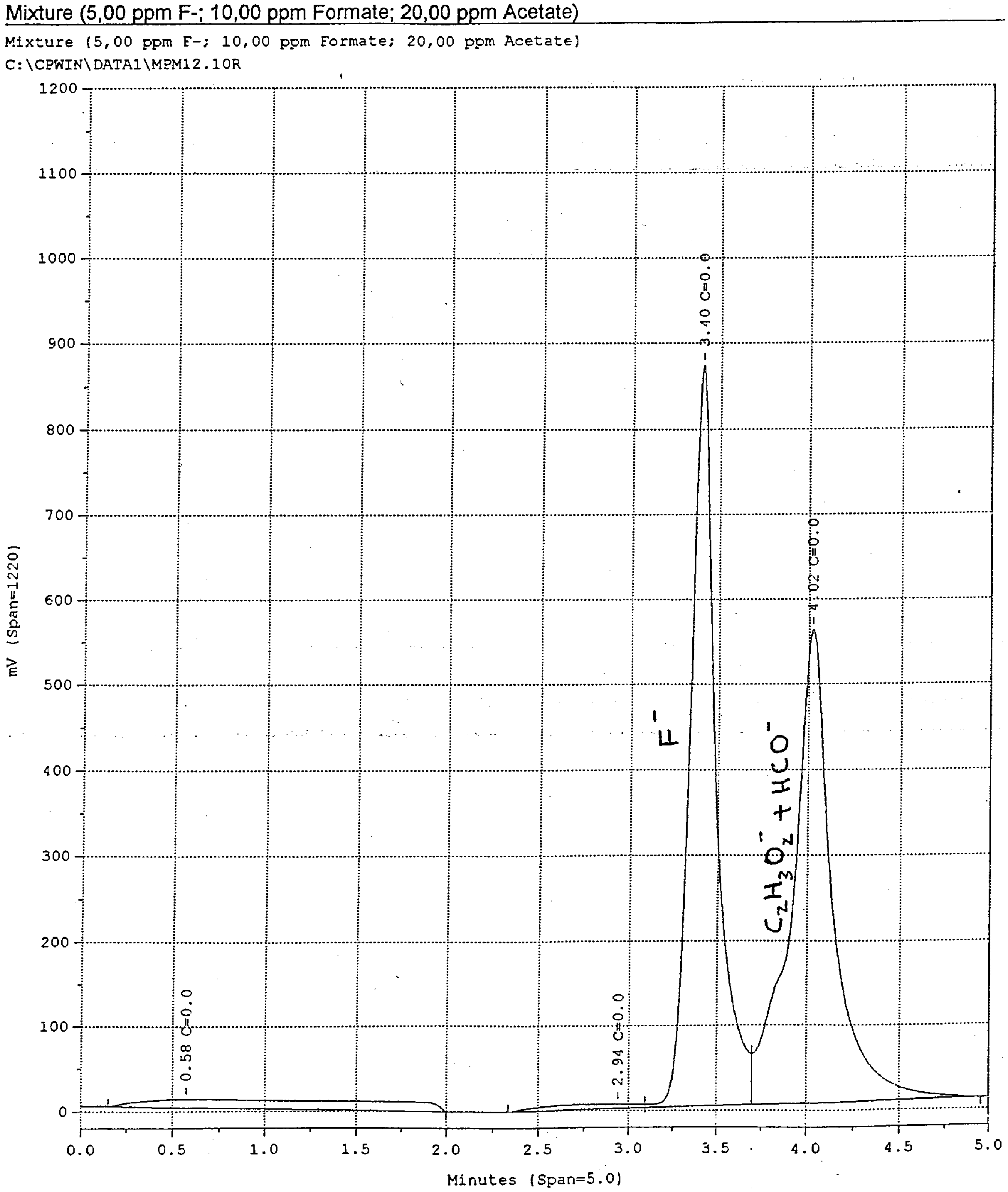


Figure 8.10: Chromatogram of a mixture whose composition is 5.00 ppm F^-,10.00 ppm formate and 20.00 ppm acetate (eluent:water = 70:30)



Sample Name: **Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)**

Figure 8.11: Chromatogram of a mixture whose composition is 5.00 ppm F^-,10.00 ppm formate and 20.00 ppm acetate (eluent:water = 30:70)

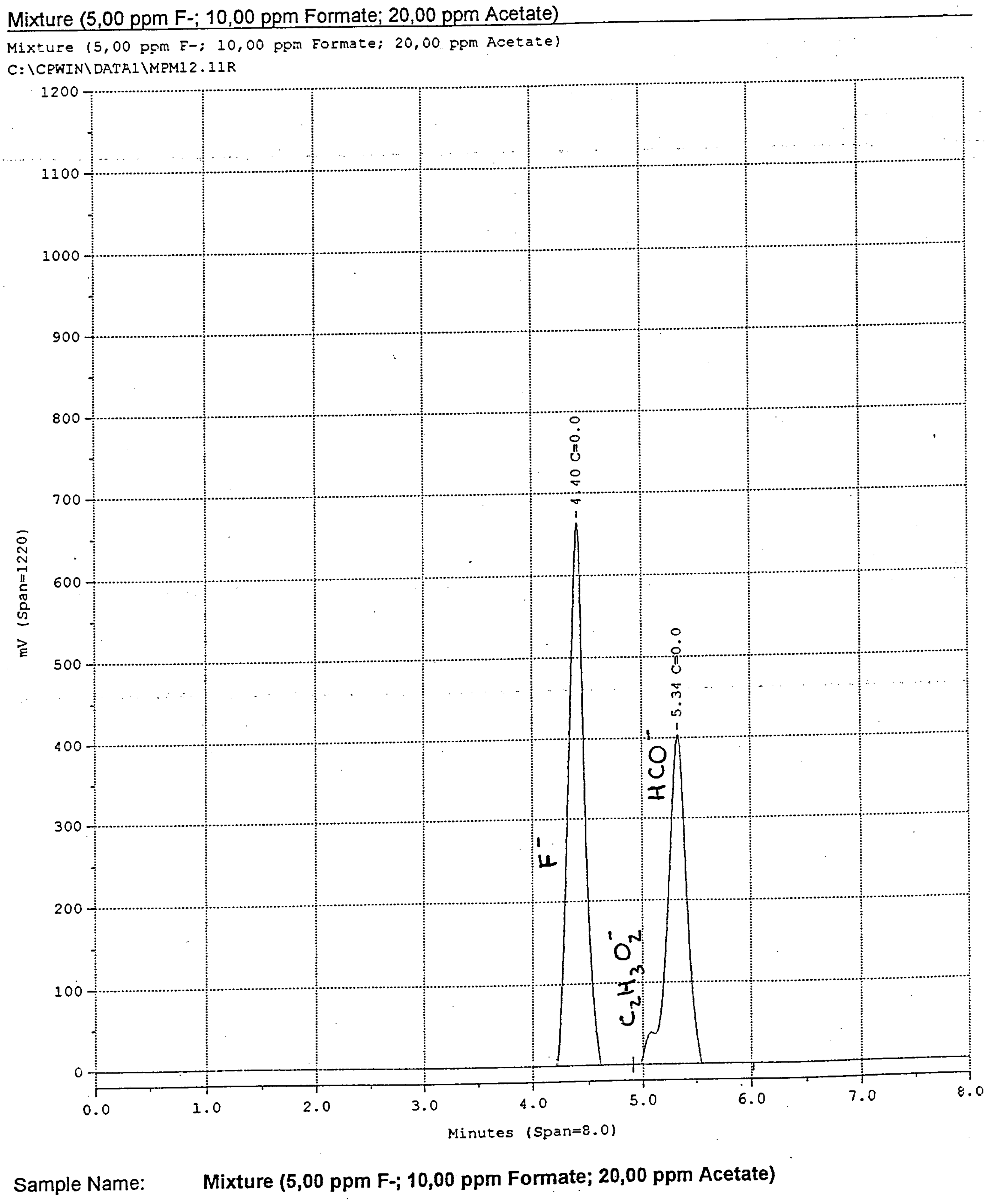
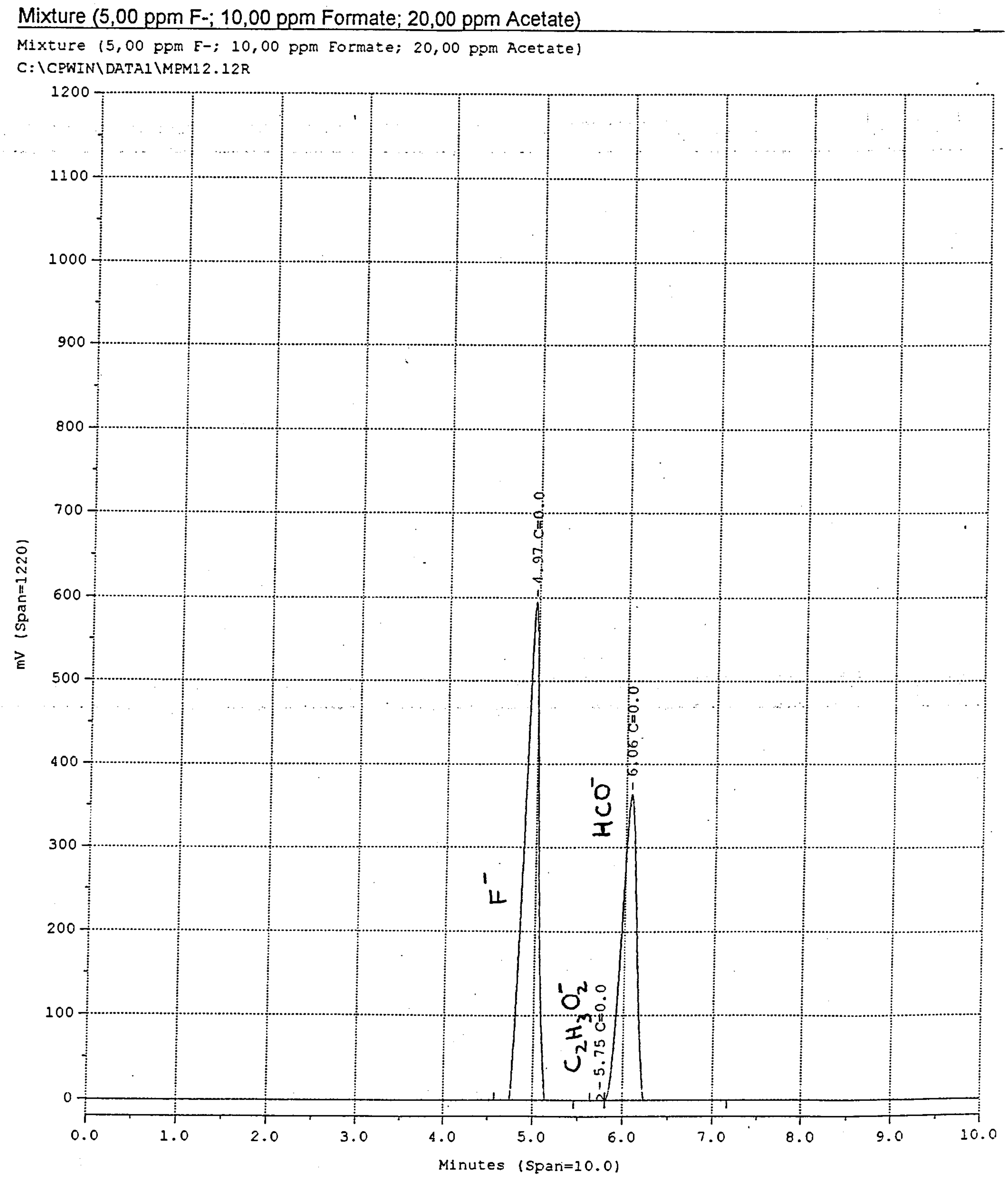


Figure 8.12: Chromatogram of a mixture whose composition is 5.00 ppm F$^-$,10.00 ppm formate and 20.00 ppm acetate (eluent:water = 20:80)


Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)

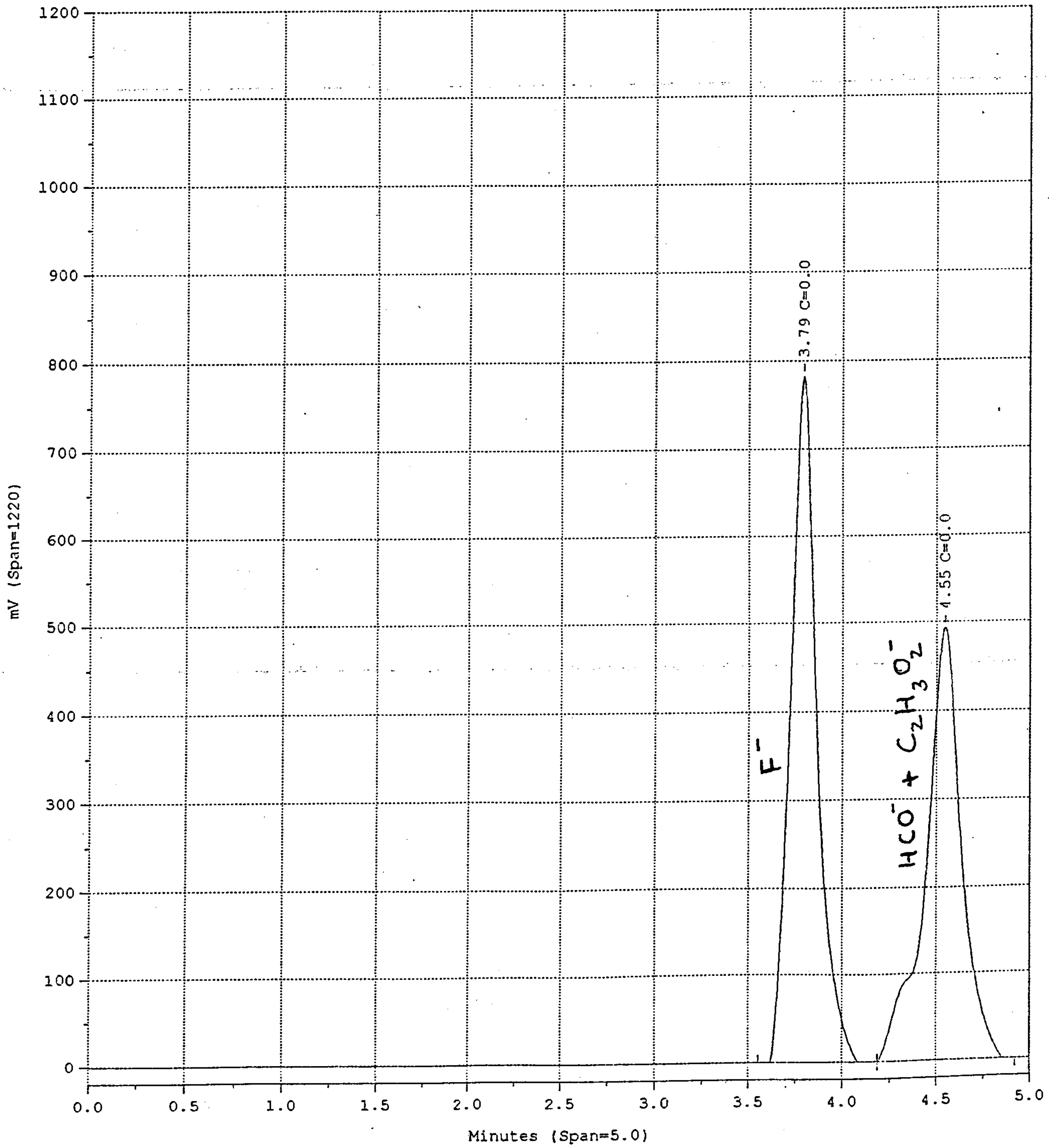
Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)
C:\CPWIN\DATA1\MPM12.12R

Sample Name: **Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)**

Figure 8.13: Chromatogram of a mixture whose composition is 5.00 ppm F$^-$,10.00 ppm formate and 20.00 ppm acetate (eluent:water = 40:60)

Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)

Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)
C:\CPWIN\DATA1\MPM12.13R



Sample Name: **Mixture (5,00 ppm F-; 10,00 ppm Formate; 20,00 ppm Acetate)**

8.7 Fluoride Analysis in Chemical gypsum Samples

The standard spiking (addition of known amount of fluoride standard) technique was used chiefly in the ion chromatographic work because the results of the ISE work had shown the amount of fluoride in the chemical gypsum samples to be low. In certain cases a normal calibration technique was used to determine the quantity of fluoride in the laboratory samples.

8.7.1 Chromatographic conditions

A commercial Dionex concentrate eluent solution was diluted tenfold to produce a mixture the composition of which was 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. This diluted solution was used as eluent. This concentration of eluent was referred to as 100 % as explained in Section 8.6.2. The sample size was fixed at 50 microlitres in each case. The suppressor unit was regenerated with 0.0251 M H_2SO_4 solution. The flow rate was 1.2 mL per minute.

8.7.2 Standard solutions

A series of fluoride standard solutions was prepared by serial dilution of the 1000 ppm fluoride stock solution.

8.7.3 Standard addition samples

A 20.00 mL quantity of the chemical gypsum sample solution (prepared as explained in 8.4.3) was pipetted into a 50.00 mL volumetric flask. This was followed by the addition of a predetermined amount of fluoride standard. The solutions were then made up to the mark with deionised water. The procedure was repeated for each of the other solutions, producing added fluoride concentrations of 1.00ppm, 2.00ppm, etc.

8.7.4 Chromatograms

The Ion Chromatograph was set up for normal operation and programmed to run the samples and standards accordingly. The output signal was integrated by means of the Chrom Perfect chromatographic software.

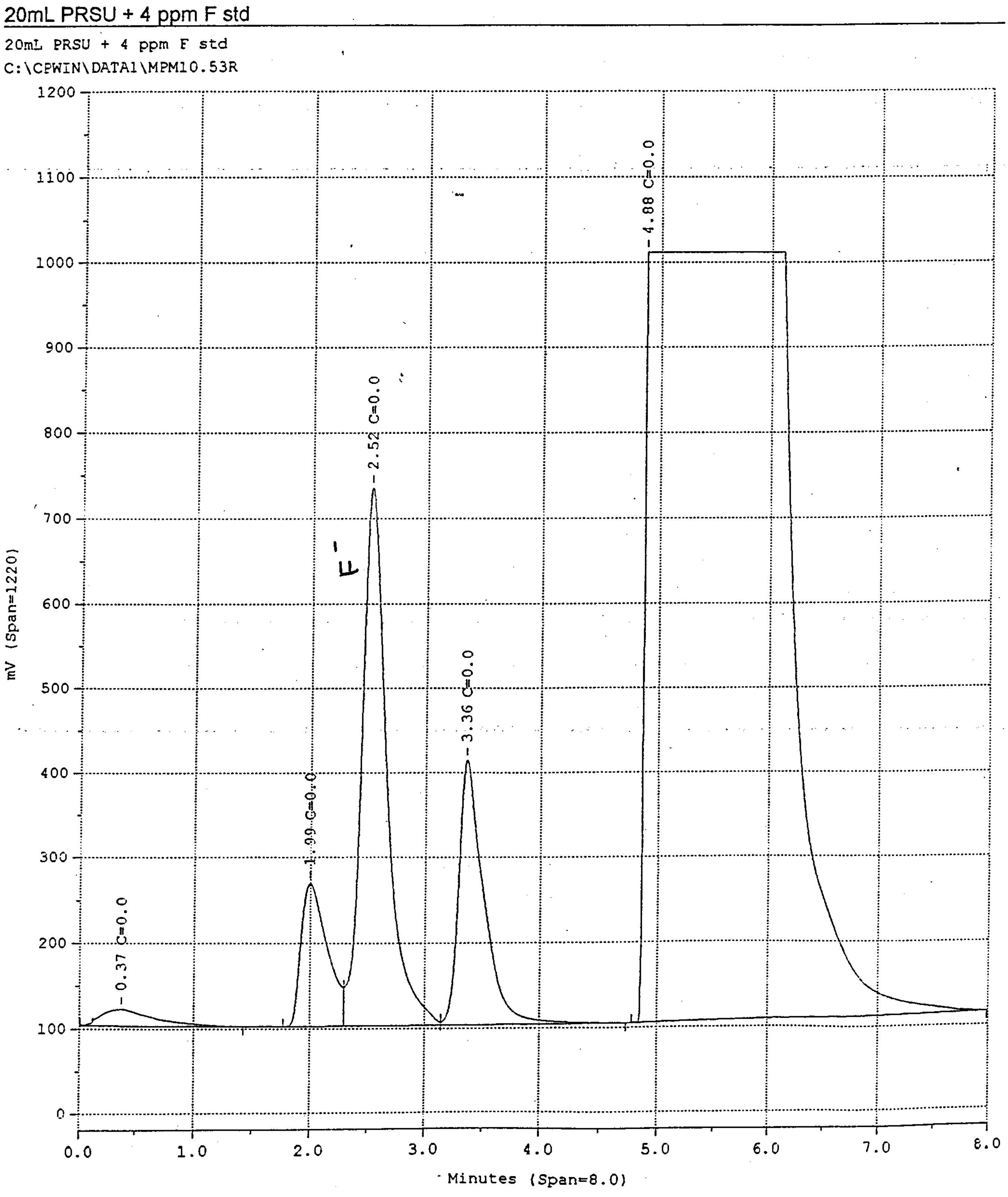
8.8 Results for PRSU rock samples

The chromatograms of retention time (minutes) versus output signal (mV) were plotted for the phosphate rock sample (PRSU). Figure 8.14 is the chromatogram for PRSU sample with added fluoride (4.00ppm).

8.8.1 Qualitative discussion of the PRSU peak information

The chromatograms for the PRSU samples generally showed three characteristic peaks between 1.5 minutes and 4 minutes, with the last very broad peak spanning ca. 4.8 minutes to 8 minutes (see Figure 8.14). The fluoride peak emerged at a retention time of 2.52 minutes for the PRSU sample. The peaks occurring at 1.99 minutes and 3.36 minutes were not identified. The broad peak was investigated and found to be a singlet emanating from one ionic species. A careful analysis of the broad peak in the PRSU sample suggested that it was due to the presence of HPO_4^{2-}.

Figure 8.14: Chromatogram of PRSU sample with added fluoride (4.00 ppm F$^-$)



Sample Name: **20mL PRSU + 4 ppm F std**

8.8.2 Quantitative results

Ideally, in order to minimize the effects of the other species on the analysis signal, calibration standards should approximate the composition of the samples to be analyzed, not only with respect to the analyte concentration, but also with regard to the concentrations of the other species in the sample matrix. When complex materials are being analyzed, the standard addition method is often helpful in counteracting the matrix effects (Skoog et al., 1997). Chemical gypsum is a complex material, hence the standard addition method was selected in order to minimize the effects of the matrix species on the analysis signal.

Willard et al.(1974) mention that the standard addition method may be used if it is known that the curve of concentration versus the analysis signal will be a straight line passing through the origin. In the standard addition method, a fixed volume of sample is transferred to a series of volumetric flasks of the same capacity. Predetermined amounts of the standard are added to each of the flasks in order to have the successive final concentrations required to derive a calibration curve. The solutions are then diluted to volume with the solvent. The measurements (detector signal) are then made for each of the mixtures of standard and sample. The calibration curve comprising concentration of standards versus the analysis signal will be a straight line which cuts the independent axis (x-axis) at a point that gives the amount of unknown in the sample of interest. However, the amount of the unknown can also be determined by firstly deriving the equation for the straight line from the calibration data. This is followed by determining the point at which the dependent variable is zero ($y = 0$). This is tantamount to interpolation of the straight line until it cuts the x-axis. This method of calculation of the amount of fluoride in the spiked samples will be used in this study.

In order to use the abovementioned method for determination of fluoride in the PRSU sample, a plot of the concentration of fluoride standards versus peak height (Table 8.5) was done to determine whether the raw data would describe a straight line passing through the origin as explained above. The plot is shown in Figure 8.15.

Table 8.5: Average peak height/peak area information for the fluoride standards

$[F^-]$ ppm	Retention Time (min)	Peak Area (PA)	Peak Height (PH)
2.00	2.66	3031580	281076.28
4.00	2.65	5932063	554650.03
5.00	2.66	6682527	688020.1
8.00	2.61	11714253.33	946211.37

The least square (the 8.00 ppm standard was excluded since it appeared to be overscale) for PH versus fluoride ion concentration (ppm) for the fluoride standards gave the equation

$$PH = 135810.6[F^-] + 9943.105$$

On the other hand, the least square fit for PA versus fluoride ion concentration (ppm) gave

$$PA = 1250305[F^-] + 630938.1$$

The anticipated concentration of fluoride for the three standards using each of the above equations yielded the results tabulated in Table 8.6.

Figure 8.15

Raw data for fluoride standards

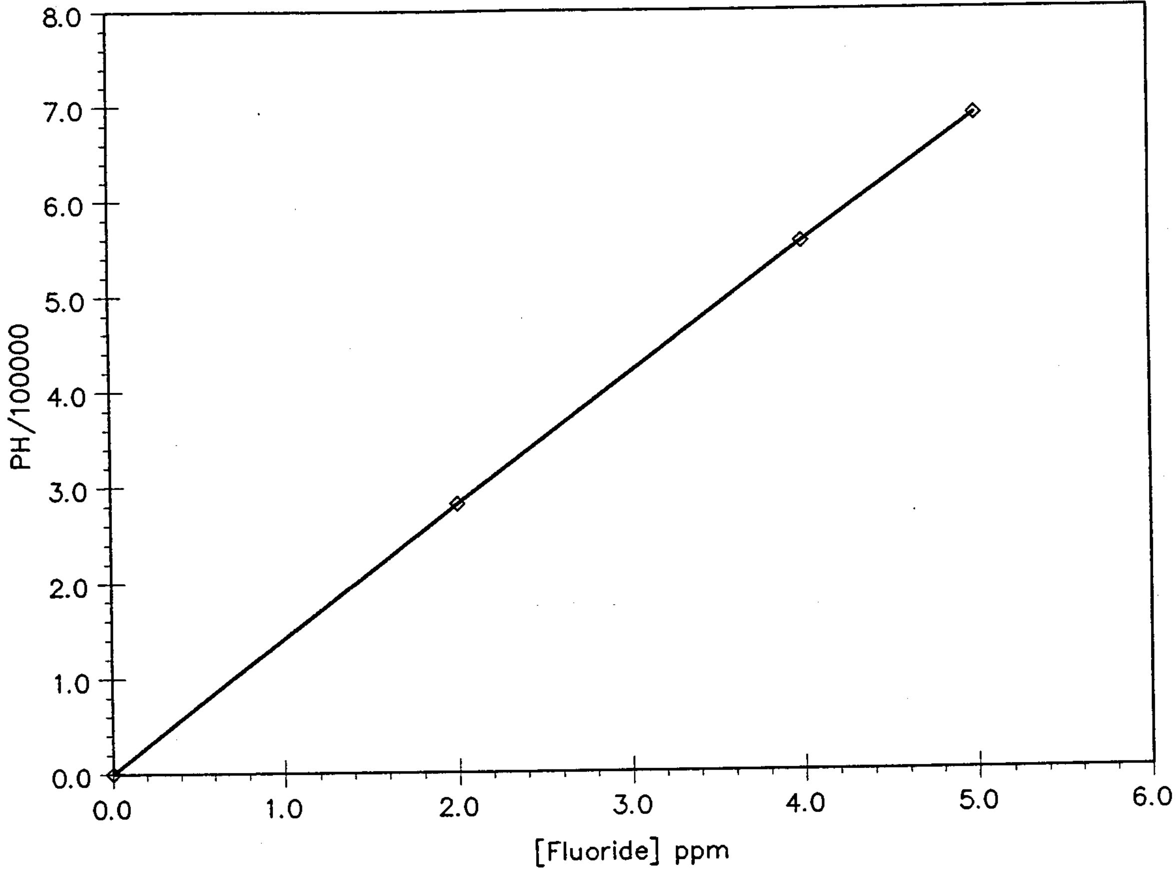


Table 8.6: Average peak height/peak area information for the fluoride standards

[F$^-$] ppm Std	Computed [F$^-$] ppm from PA data	Computed [F$^-$] ppm from PH data
2.00	1.92	2.00
4.00	4.23	4.01
5.00	4.84	4.99

Clearly, the peak height data was more accurate than the peak area data in this particular case. The peak height approach was utilized in the subsequent data handling work.

Standard addition data analysis

The peak data for each of the samples and standard mixtures analyzed is given in Table 8.7.

Table 8.7: Average peak height information for the standard addition mixtures

Sample + standard (Total vol = 50.00 mL)	Retention Time (min) of replicates	Average Peak Height (PH)
20.00 mL PRSU + 2.00 ppm F$^-$ std	2.51;2.52; 2.51	419827.13
20.00 mL PRSU + 4.00 ppm F$^-$ std	2.52; 2.51; 2.51	602155.3
20.00 mL PRSU + 5.00 ppm F$^-$ std	2.52; 2.52; 2.53	694689.93
20.00 mL PRSU + 8.00 ppm F$^-$ std	2.50	Plateau*

*NB: Plateau means the peak is off scale and thus flattens.

Using the Willard et al. method described above, the least squares line equation for the data given in Table 8.7 was

$$PH = 91841.38[F^-] + 236805.7$$

The standard deviation of the slope, s_m, was computed to be 339. The standard deviation of the intercept, s_b, was 1313. The standard deviation about the measurement, s_r, was 734. The correlation coefficient was determined to be 1.00. Graphically, the average fluoride ion concentration can be obtained by interpolation until the straight line cuts the concentration axis (x-axis) of the calibration curve. By calculation, the concentration of fluoride is obtained from the calibration curve as

$$[F^-] = \left|\frac{-236805.7}{91841.38}\right| = 2.58\,ppm$$

Taking the dilution effects into account, the fluoride ion concentration in PRSU was

$$\begin{aligned}[F^-] &= 2.58\ ppm \times \frac{50.00\,mL}{20.00\,mL} \\ &= 6.45\ ppm\end{aligned}$$

8.9 Results for Kynoch filter pan samples

The samples used were the Filter Pan Samples labelled FPSU (unwashed), FPSW (water washed), and FPSL (lime washed). The source of these samples has already been described in Sections 8.4.1 and 8.4.3.3 above.

8.9.1 FPSU samples

The chromatograms consisting of retention time (minutes) versus output signal (mV) were plotted for each sample analyzed. Typical examples are given in the chromatogram shown in Figure 8.16, which represents a 10 minute run of the sample with added fluoride concentration of 1.00 ppm, and the chromatogram given in Figure 8.17, which represents a 5 minute run of the sample with added fluoride concentration of 4.00 ppm. The fluoride peak occurs at a retention time of 2.80 minutes in each of these chromatograms. The software integration of the chromatographic peaks was done automatically from baseline to baseline. The peak data for each of the FPSU (unwashed) samples and standards mixture analyzed are given in Table 8.8.

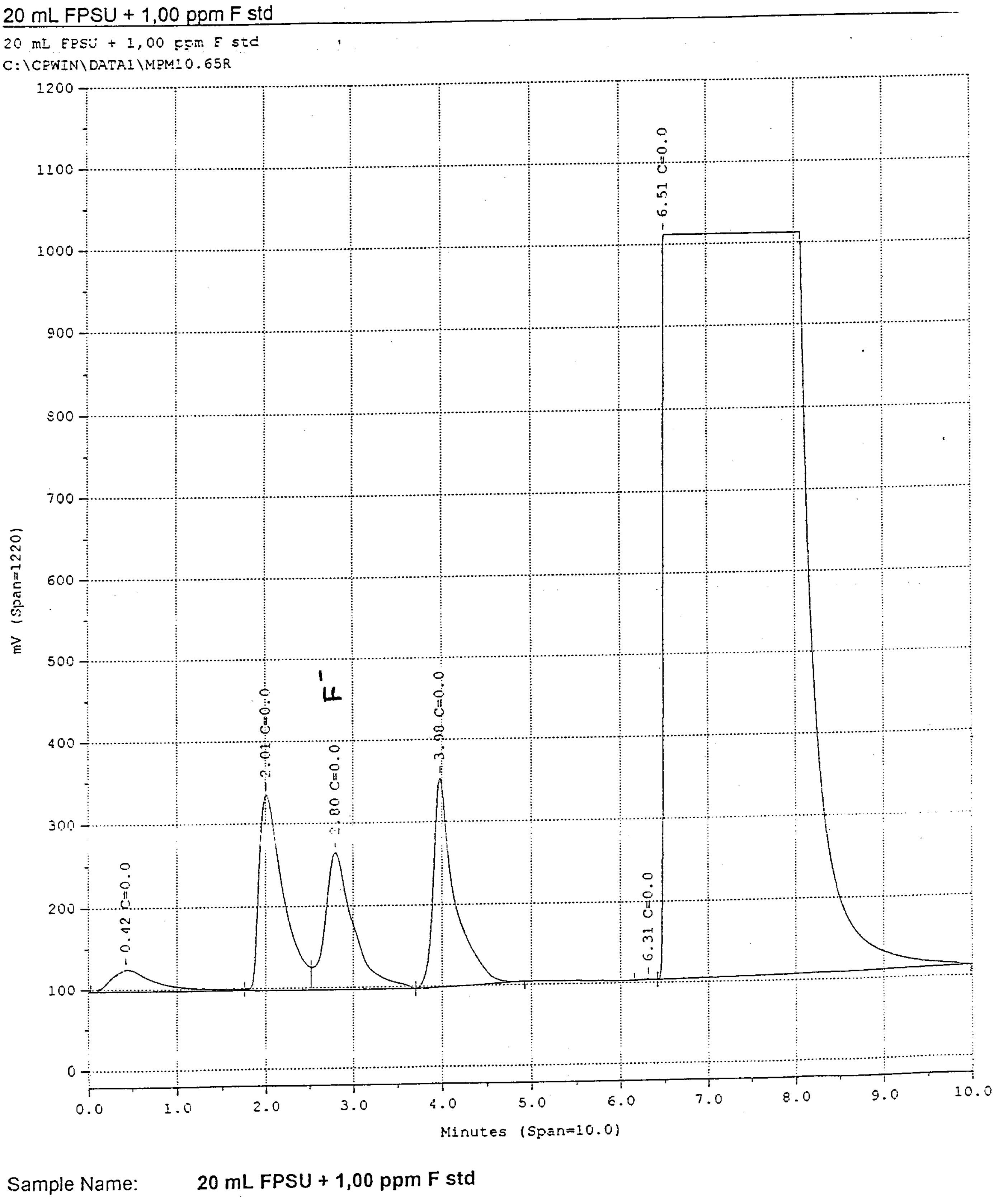
Table 8.8: Average peak height information for the standard addition mixtures for FPSU sample

FPSU Sample + standard (Total vol = 50.00 mL)	Retention Time (min) of replicates	Average Peak Height (PH)
20.00 mL FPSU + 1.00 ppm F^- std	2.80;2.80; 2.80	168532
20.00 mL FPSU + 2.00 ppm F^- std	2.80; 2.81; 2.81	277425
20.00 mL FPSU + 3.00 ppm F^- std	2.80; 2.81; 2.80	325317
20.00 mL FPSU + 4.00 ppm F^- std	2.83; 2.80; 2.80	391925

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.8. The equation was

$$PH = 74807[F^-] + 96282$$

Figure 8.16: Chromatogram of FPSU sample with added fluoride (1.00 ppm F$^-$)

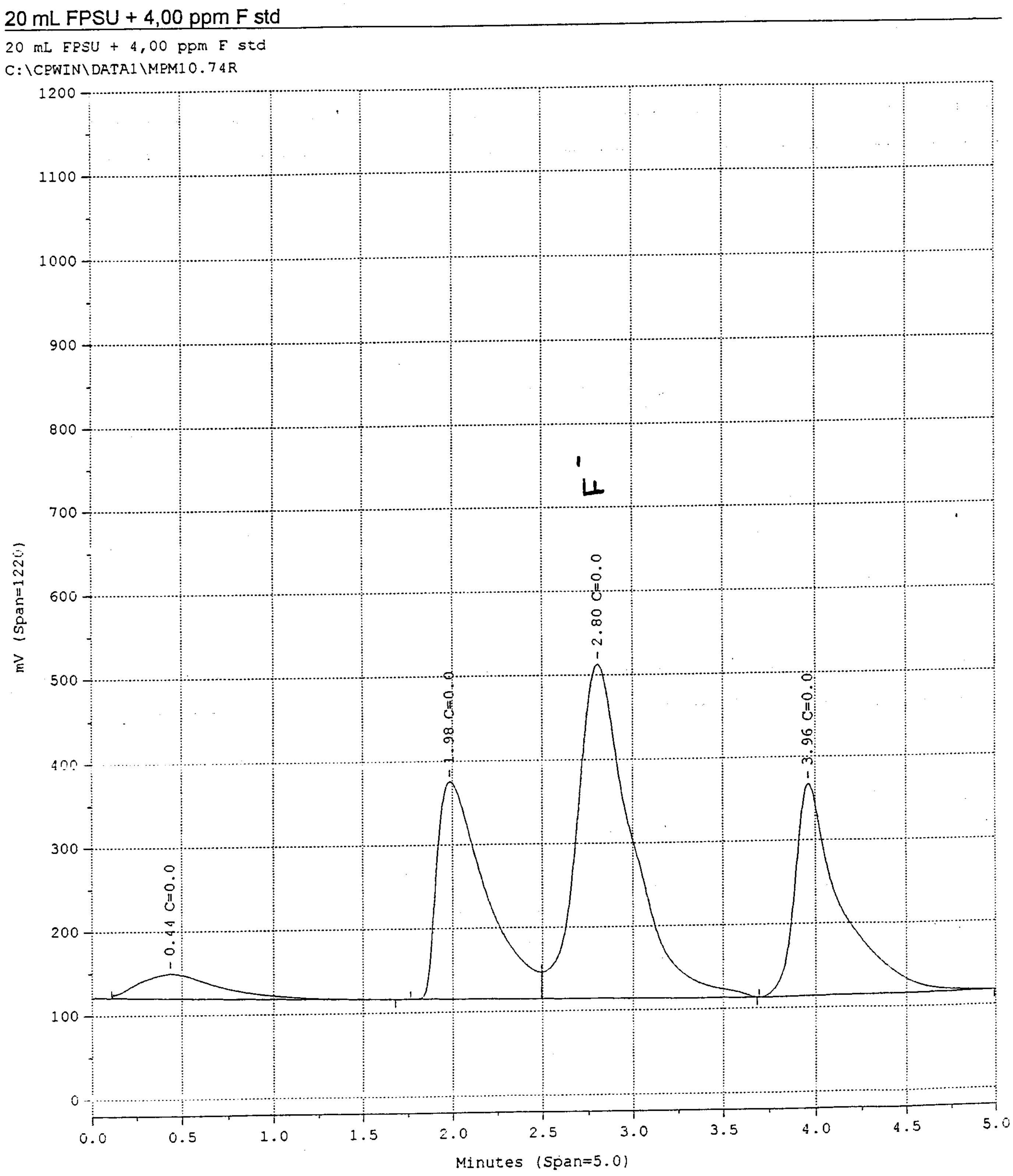


20 mL FPSU + 1,00 ppm F std

20 mL FPSU + 1,00 ppm F std
C:\CPWIN\DATA1\MPM10.65R

Sample Name: **20 mL FPSU + 1,00 ppm F std**

Figure 8.17: Chromatogram of FPSU sample with added fluoride (4.00 ppm F$^-$)



Sample Name: **20 mL FPSU + 4,00 ppm F std**

The standard deviation of the slope, s_m, was computed to be 2074. The standard deviation of the intercept, s_b, was 5680. The standard deviation about the measurement, s_r, was 4638. The correlation coefficient was determined to be 0.999.

The computed average fluoride ion concentration in the prepared FPSU sample was obtained as described previously (Section 8.8.2) and was determined to be 1.29 ppm. Taking dilution effects into account, the fluoride concentration in the original sample of FPSU was 3.22 ppm.

8.9.2 FPSW samples

A summary of the peak height data is given in Table 8.9. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.9: Average peak height information for the standard addition mixtures (FPSW sample)

FPSW Sample + standard (Total vol = 50.00 mL)	Retention Time (min) of replicates	Average Peak Height (PH)
20.00 mL FPSW + 1.00 ppm F^- std	2.79;2.79; 2.80	100949
20.00 mL FPSW + 2.00 ppm F^- std	2.80; 2.79	179485
20.00 mL FPSW + 3.00 ppm F^- std	2.85; 2.80; 2.80	241539
20.00 mL FPSW + 4.00 ppm F^- std	2.80; 2.80	329817

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation which was derived from the data in Table 8.9. The equation was

$$PH = 74865[F^-] + 25783$$

The standard deviation of the slope, s_m, was computed to be 3390. The standard deviation of the intercept, s_b, was determined to be 9284. The standard deviation about the measurement, s_y, was 7580. The correlation coefficient was 0.998.

The computed average fluoride ion concentration in the prepared FPSW sample was obtained as described in Section 8.8.2, and determined to be 0.34 ppm. Taking dilution effects into account, the fluoride concentration in the original sample of FPSW was 0.85 ppm.

8.9.3 FPSL samples

The peak data is summarised in Table 8.10. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.10: Average peak height information for the standard addition mixtures (FPSL sample)

FPSL Sample + standard (Total vol = 50.00 mL)	Retention Time (min) of replicates	Average Peak Height (PH)
20.00 mL FPSL + 1.00 ppm F^- std	2.81;2.81; 2.81	161741
20.00 mL FPSL + 2.00 ppm F^- std	2.81; 2.81; 2.82	242258
20.00 mL FPSL + 3.00 ppm F^- std	2.82; 2.81; 2.82	320458
20.00 mL FPSL + 4.00 ppm F^- std	2.82; 2.81; 2.82	400203

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.10. The equation was

$$PH = 79358.6[F^-] + 82768.5$$

The standard deviation of the slope, s_m, was computed to be 299. The standard deviation of the intercept, s_b, was 819. The standard deviation about the measurement, s_r, was 669. The correlation coefficient was determined to be 1.00. The average fluoride ion concentration in the prepared FPSL sample was obtained as described in Section 8.8.2, and determined to be 1.04 ppm. Taking dilution effects into account the fluoride concentration in the original sample of FPSL was 2.60 ppm.

8.10 Kynoch Stockpile (SDS) samples

The samples used were obtained from the phosphogypsum stockpile and labelled Slime Dam Samples or SDSU (unwashed). The source of the samples was discussed above in Section 8.4.1. The pretreated samples labelled water washed (SDSW) and lime washed (SDSL) were prepared as explained in Section 8.4.3.

8.10.1 SDSU samples

The peak data is summarized in Table 8.11. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.11: Average peak height information for the standard addition mixtures (SDSU)

SDSU Sample + standard (Total vol = 50.00 mL)	Retention Time (min)	Peak Height (PH)
20.00 mL SDSU + 1.00 ppm F^- std	2.80;2.79; 2.80; 2.80	197347
20.00 mL SDSU + 2.00 ppm F^- std	2.80; 2.80; 2.80	256403
20.00 mL SDSU + 4.00 ppm F^- std	2.85; 2.81; 2.80	408947
20.00 mL SDSU + 6.00 ppm F^- std	2.81; 2.81; 2.81	552887

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.11. The equation was

$$PH = 72041.69[F^-] + 119760.5$$

The standard deviation of the slope, s_m, was computed to be 1726. The standard deviation of the intercept, s_b, was 6517. The standard deviation about the measurement, s_r, was 6630. The correlation coefficient was determined to be 0.999.

The computed average fluoride ion concentration in the prepared SDSU sample was obtained as described in Section 8.8.2, and determined as 1.66 ppm. Taking the dilution effects into account, the concentration of fluoride in the sample was 4.15 ppm.

8.10.2 SDSW samples

The peak data for each of the SDSW (water washed) samples and standards mixture analyzed are given in Table 8.12. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.12: Average peak height information for the standard addition mixtures (SDSW)

SDSW Sample + standard (Total vol = 50.00 mL)	Retention Time (min) for each replicate	Average Peak Height (PH)
20.00 mL SDSW + 1.00 ppm F^- std	2.74;2.74; 2.74	153903
20.00 mL SDSW + 2.00 ppm F^- std	2.75; 2.74; 2.75	219348
20.00 mL SDSW + 4.00 ppm F^- std	2.75; 2.75; 2.75	364276
20.00 mL SDSW + 6.00 ppm F^- std	2.75; 2.77; 2.75	500115

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in the Table 8.12. The equation was

$$PH = 69698.75[F^-] + 82889.58$$

The standard deviation of the slope, s_m, was computed to be 782. The standard deviation of the intercept, s_b, was 2950. The standard deviation about the measurement, s_r, was 3001. The correlation coefficient was determined to be 1.00.

The computed average fluoride ion concentration in the prepared SDSW sample was 1.19 ppm. Taking into account the dilution effects, the actual fluoride ion concentration in SDSW was 2.98ppm.

8.10.3 SDSL samples

The peak data for each of the SDSL (lime washed) samples and standards mixture analyzed is given in Table 8.13. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.13: Average peak height information for the standard addition mixtures (SDSL)

SDSL Sample + standard (Total vol = 50.00 mL)	Retention Time (min) for each replicate	Average Peak Height (PH)
20.00 mL SDSL + 1.00 ppm F^- std	2.79;2.79; 2.80	149687
20.00 mL SDSL + 2.00 ppm F^- std	2.79; 2.79; 2.80	228605
20.00 mL SDSL + 4.00 ppm F^- std	2.80; 2.80; 2.80	405649
20.00 mL SDSL + 6.00 ppm F^- std	2.80; 2.80; 2.80	569818

The concentration of the fluoride ion in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.13. The equation was

$$PH = 84656.56[F^-] + 63305.93$$

The standard deviation of the slope, s_m, was computed to be 1088. The standard deviation of the intercept, s_b, was 4108. The standard deviation about the measurement, s_r, was 4180. The correlation coefficient was determined to be 1.00.

The computed average fluoride ion concentration in the SDSL sample was determined to be 0.75 ppm, as described previously in Section 8.8.2. Taking the dilution effects into account, the fluoride ion concentration in SDSL was 1.89 ppm.

8.11 Results for Tioxide titangypsum samples

The samples used were the Tioxide Chemical Gypsum, labelled TCGU (unwashed), TCGW (water washed), and TCGL (lime washed). All samples were prepared and chromatographed under the conditions set out in Section 8.4.3. The sampling data was given previously in Table 8.2

8.11.1 TCGU samples

The peak data is summarized in Table 8.14. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.14: Average peak height information for the standard addition mixtures (TCGU)

TCGU Sample + standard (Total vol = 50.00 mL)	Retention Time (min) for each replicate	Average Peak Height (PH)
20.00 mL TCGU + 2.00 ppm F^- std	2.80;2.80; 2.80	163436
20.00 mL TCGU + 4.00 ppm F^- std	2.80; 2.79; 2.80	322847
20.00 mL TCGU + 6.00 ppm F^- std	2.80; 2.79; 2.80	475463
20.00 mL TCGU + 7.00 ppm F^- std	2.80; 2.79; 2.80	547118

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.14. The equation was

$$PH = 76865.08[F^{-}] + 12106.85$$

The standard deviation of the slope, s_m, was computed to be 1016.5. The standard deviation of the intercept, s_b, was 5207.9. The standard deviation about the measurement, s_r, was 3903.9. The correlation coefficient was determined to be 1.00.

The computed average fluoride ion concentration in the TCGU sample was obtained as described previously in Section 8.8.2 and found to be 0.16 ppm. Taking the dilution effects into account, the original fluoride ion concentration in TCGU was 0.40 ppm.

8.11.2 TCGW samples

The peak data is summarized in Table 8.15. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.15: Average peak height information for the standard addition mixtures (TCGW)

TCGW Sample + standard (Total vol = 50.00 mL)	Retention Time (min) for each replicate	Average Peak Height (PH)
20.00 mL TCGW + 2.00 ppm F^- std	2.80;2.81; 2.81	163641
20.00 mL TCGW + 4.00 ppm F^- std	2.80; 2.80; 2.80	313494
20.00 mL TCGW + 6.00 ppm F^- std	2.81; 2.80; 2.80	469849
20.00 mL TCGW + 7.00 ppm F^- std	2.85; 2.80; 2.81	522377

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.15. The equation was

$$PH = 73052.63[F^{-}] + 20340.27$$

The standard deviation of the slope, s_m, was computed to be 2738. The standard deviation of the intercept, s_b, was 14027. The standard deviation about the measurement, s_r, was 10515. The correlation coefficient was determined to be 1.00.

The computed average fluoride ion concentration in TCGW sample was obtained as described previously in Section 8.8.2 and found to be 0.28 ppm. Taking into account the dilution effects, the original fluoride ion concentration in TCGW was 0.70 ppm.

8.11.3 TCGL samples

The peak data is summarized in Table 8.16. The software integration of the chromatographic peaks was done automatically from baseline to baseline.

Table 8.16: Average peak height information for the standard addition mixtures (TCGL)

TCGL Sample + standard (Total vol = 50.00 mL)	Retention Time (min) for each replicate	Average Peak Height (PH)
20.00 mL TCGL + 2.00 ppm F^- std	2.79;2.79; 2.79	162285
20.00 mL TCGL + 4.00 ppm F^- std	2.79; 2.79	311596
20.00 mL TCGL + 6.00 ppm F^- std	2.80; 2.80; 2.80	466505
20.00 mL TCGL + 7.00 ppm F^- std	2.79; 2.79	541833

The concentration of fluoride in each of the standard addition mixtures was computed from the least square fit given by the equation derived from the data in Table 8.16. The equation was

$$PH = 76086.42[F^-] + 9144.237$$

The standard deviation of the slope, s_m, was computed to be 421.5. The standard deviation of the intercept, s_b, was 2159. The standard deviation about the measurement, s_r, was 1619. The correlation coefficient was 1.00.

The computed average fluoride ion concentration in the prepared TCGL sample was obtained as described previously in Section 8.8.2 and found to be 0.12 ppm. Taking into account the dilution effects, the original fluoride ion concentration in TCGL was 0.30 ppm.

8.12 Percentage fluoride for Kynoch and Tioxide samples

The results obtained above for the ion chromatographic method, for both Kynoch batch 3 and Tioxide batch 1samples, were expressed as percentages with the uncertainties in the fluoride concentration determined by means of equation 6.16. The results are summarized in Table 8.17. The corresponding ion selective electrode method results for the same samples are also given for purposes of comparison.

Table 8.17: Summary of ISE results versus IC results

Sample	IC method %F$^-$	ISE method %F$^-$
PRSU	0.258±0.019%	0.266±0.005%
FPSU	0.129±0.010%	0.104±0.000%
FPSW	0.034±0.016%	0.008±0.000%
FPSL	0.104±0.001%	0.101±0.005%
SDSU	0.166±0.013%	0.133±0.005%
SDSW	0.119±0.006%	0.091±0.005%
SDSL	0.077±0.007%	0.107±0.005%
TCGU	0.016±0.008%	0.008±0.000%
TCGW	0.028±0.024%	0.000±0.000%
TCGL	0.012±0.004%	0.000±0.000%

8.13 Discussion of results

A close scrutiny of the fluoride peak from each of the chromatograms of the chemical gypsum samples analyzed indicates a bit of tailing (see fluoride peak with retention time of 2.80 minutes in chromatogram given in Figure 8.16). The fluoride peak is also fused to a small extent with the preceding peak which occurs at a retention time of 2.01 minutes. Integrators and computers separate fused peaks by dropping perpendiculars from the valley between them or by skimming a tangent below a peak that is very small compared to the one to which it is fused (Dyson, 1990). In Figure 8.16, a perpendicular has been used by the computer to separate the fused peaks. The use of perpendiculars to separate two overlapping peaks will give rise to inaccuracies in area measurements unless the peaks are of the same height and width and are symmetrical in shape, or if the valley is no more than 5% of the peak height (Dyson, 1990). Peak height is also affected by fused peaks. If a small peak occurs on the tail of a larger peak, there may be some error in the height measurement (Dyson, 1990).

The amount of fluoride in the phosphate rock sample (PRSU) was determined by the IC method as 0.258 %±0.019%(m/m). The water washed filter pan samples contained 74 % less fluoride than the unwashed samples. Lime treated filter pan samples contained 19% less fluoride than the unwashed samples. The water purification treatment was therefore better than the lime treatment for the filter pan samples. The SDS samples, which had been collected from a stockpile (stack) which was over seven years old (exposed to natural elements such as rain etc.), contained 0.166 %±0.013%(m/m) fluoride. The TCG samples proved to contain a minute amount of fluoride with a maximum of 0.016 % ±0.008%(m/m).

The results obtained by the Ion Chromatography method, as summarized from Table 8.17, generally exhibited a higher uncertainty as compared to those obtained by the Ion Selective Electrode method. This trend is more evident for samples whose fluoride content is very low such as FPSW, TCGU, TCGW and TCGL.

As stated in Section 8.1, all samples analyzed by the ion chromatography method were also analyzed with the ion selective electrode method in order to test whether the two methods would agree or not. For the ISE method, the fluoride content in each sample was determined using the direct ion concentration mode. Judging from the results in Table 8.17, both methods, ISE and IC, corroborated each other's results for samples whose fluoride content is approximately 0.100% (m/m) fluoride or more.

Chapter 9 Determination of fluoride by the Willard and Winter method

9.1 Introduction

During the 1960s fluoride was separated by the Willard and Winter steam-distillation method and then determined by a titration procedure (Willard and Winter, 1933). The Willard and Winter method is the standard method of determination of fluoride in inorganic materials (Scott, 1979; Peters and Ladd, 1971). This method has been explained in detail in Section 2.2.3.

In this study, the standard Willard and Winter method was applied to recover fluoride in chemical gypsum samples. The fluoride content in the chemical gypsum samples was subsequently determined by a potentiometric titration as well as by spectrophotometric analysis. Using the equipment available in this study, the potentiometric method proved to have limitations when dealing with the low levels of fluoride in the chemical gypsum samples.

9.2 Experimental

9.2.1 Kynoch batch 3 phosphogypsum sample

A 0.2560g mass of Kynoch phosphogypsum sample was transferred into a platinum crucible, and a flux consisting of 5g of 1:1 Na_2O_2-Na_2CO_3 mixture was added. Fusion was effected in a muffle furnace by gradually increasing the temperature through the stages 21 °C → 107 °C → 300 °C → 600 °C → 900 °C. This gradual increase in temperature is a modification of the Peters and Ladd method explained in Section 2.1.1. The modification was effected as a safety precaution because the original Peters and Ladd method used a hot Méker burner flame. The temperature was maintained at 900 °C for 30 minutes. The cold melt was transferred to a 250 mL distillation flask and the crucible rinsed with 50 mL of concentrated sulphuric acid. A 0.75g quantity of finely ground quartz sand was added and the flask connected to the distillation apparatus. Steam distillation occurred in an oil bath at a temperature held between 140 –150 °C, until about 150mL of the distillate had been collected. The distillate was transferred to a 250 mL volumetric flask and made up to the mark with deionised water.

9.2.2 Tioxide titangypsum (TCG) batch 1 sample

A 0.2574g mass of titangypsum sample was transferred to a platinum crucible. The sample was prepared as for the Kynoch sample, as described above. Omnia phosphogypsum samples were not collected from the plant as it was thought that, should the standard method corroborate or render the results for the ISE and IC methods using Kynoch phosphogypsum and Tioxide titangypsum invalid, this would be sufficient to validate or put into question the efficiency of these methods. Hence, the two chemical gypsum samples, Kynoch phosphogypsum and Tioxide titangypsum, were considered sufficient.

9.2.3 Fluoride Analysis – A potentiometric approach

Since the levels of fluoride in both Kynoch and Tioxide chemical gypsums had already been proved to be low (Chapter 7 and 8), it was decided that a potentiometric endpoint detection be utilized instead of the visual indicator, as practiced for the Th-Alizarine method (Section 2.2.3). The decision was based on the advantage of automated potentiometric titration over the conventional visual volumetric titration when it comes to titration of dilute solutions. A back-titration approach described in Scott's standard methods of chemical analysis as Offerman's method was applied (Scott, 1979).

9.2.3.1 Apparatus

Metrohm AutoTitrator, comprising Potentiograph E 576, Dosimat E575 and stirrer unit E 549, all by Metrohm Herisau.

9.2.3.2 Procedure for standardization of HCl

A dilute solution of hydrochloric acid was prepared to be approximately 0.05M from a concentrated reagent. Anhydrous sodium carbonate was dried in an oven for two hours at 120 °C and then allowed to cool in a desiccator. A 1.4013g mass of the dried sodium carbonate was transferred into a 250mL volumetric flask, dissolved and brought up to the mark with deionized water. A 5.00 mL aliquot of the sodium carbonate solution was titrated with the dilute hydrochloric acid solution. The titration was performed in triplicate.

9.2.3.2.1 Results

Data from the titration curve for the first replicate are summarized in Table 9.1.

From the titration data (Table 9.1), the second derivative method gave the endpoint volume as

$$[Vol]_{endpt} = \frac{(9.3412 + 9.439528)}{2} = 9.390364 \approx 9.39\,mL\,.$$

The endpoint volumes for the second and third replicate gave the same value of 9.49 mL. The concentration of the NaC$_2$O$_3$ solution was determined from the weighed mass to be

$$[Na_2CO_3] = \frac{1.4013g \times 1000mL\,/\,L}{105.98874g\,/\,mol \times 250mL} = 0.0529\,M\,.$$

Table 9.1: Data from titration curve for HCl secondary standard solution

Raw data Vol (mL)	Raw data pH	1st derivatives from C data vs D data		Second derivatives from E data vs F data	
A	B	C	D	E	F
Vol (mL)	pH	DpH/DVol	Vol (mL)	D^2pH/DVol^2	Vol (mL)
8.3579154	6.2903226				
8.8495575	5.9032258	-0.787355	8.6037365		
8.9478859	5.8064516	-0.984194	8.8987217	-0.667283	8.7512291
9.0462144	5.6935484	-1.148226	8.9970501	-1.668208	8.9478859
9.1445428	5.5806452	-1.148226	9.0953786	9.259e-14	9.0462144
9.2428712	5.3709677	-2.132419	9.193707	-10.00925	9.1445428
9.3411996	4.9677419	-4.100806	9.2920354	-20.0185	9.2428712
9.439528	4.000000	-9.841935	9.3903638	-58.38728	9.3411996
9.5378564	3.1612903	-8.529677	9.4886922	13.345665	9.439528
9.6361849	2.983871	-1.804355	9.5870206	68.396531	9.5378564
9.7345133	2.8387097	-1.47629	9.6853491	3.3364161	9.6361849
9.8328417	2.7096774	-1.312258	9.7836775	1.6682081	9.7345133
10.324484	2.4354839	-0.55771	10.078663	2.557919	9.9311701
10.816126	2.2903226	-0.295258	10.570305	0.5338266	10.324484

NB: The data in Table 9.1was derived from a QuattroPro calculation from the number of blocks obtained from the chart paper. For pH scale, 10 blocks were equal to 1.6129 pH units. For volume scale, 10 blocks were equal to 0.983284 mL. The data was computer generated, hence the numbers consisted of many digits.

Stoichiometrically, the reaction between carbonate and HCl is

$$2H_3O^+ + CO_3^{2-} \rightarrow CO_2 + 3H_2O$$

Hence, the concentrations of the carbonate/HCl titration pair and their respective volumes could be related as

$$2[CO_3^{2-}] \times v_{CO_3^{2-}} = [H_3O^+] \times v_{H_3O^+}$$

By substituting the experimental data into the above equation the mean concentration of hydrochloric acid for the three replicates was detrmined to be $(5.59\pm0.03)\times10^{-2}$M.

The standardized hydrochloric acid solution was used as a secondary standard to determine the concentration of NaOH. The standardized NaOH solution was subsequently used in the back-titration reaction for fluoride analysis.

9.2.3.3 Procedure for standardization of NaOH solution with secondary standard HCl

A 0.1M NaOH solution was prepared. The solution was potentiometrically standardized with the secondary standard hydrochloric acid solution. The titration curve data was treated with the second derivative method as explained above, and subsequently produced endpoint volumes of 9.64 mL and 9.73 mL for the two standard HCl replicates respectively. These endpoint volumes have been rounded off to two decimal places, but in the calculations actual computer generated endpoint volumes were used without any rounding off.

From the reaction stoichiometry between HCl and NaOH

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

the concentration of NaOH solution was computed to be $(1.08 \pm 0.01)\text{x}10^{-1}$M. using volume data obtained directly by the second derivative method from computer generated values (with no rounding off) similar to those obtained in Table 9.1.

9.2.3.4 Percentage of fluoride in various chemical gypsum samples

Each sample of chemical gypsum (Kynoch and TCG) was prepared by pipetting 20.00 mL of the distilled sample (prepared as in 9.2.1 and 9.2.2) into a 50 mL volumetric flask followed by the addition of a 25.00 mL solution of the standardized NaOH solution which was then made up to the mark with deionized water. The titration of excess NaOH was carried out on 10.00 mL aliquots.

- Tioxide chemical gypsum (TCG) sample

The endpoint volume of the hydrochloric acid secondary standard solution required to back-titrate the excess NaOH solution was obtained from the second derivative method, as explained previously in Section 9.2.3.3. The computer generated values of the titres were 9.685349 mL, 9.685349 mL and 9.783677mL for the three replicates respectively. The average titre for the TCG samples was 9.72 ± 0.05 with RSD of 0.5%.

In order to perform the calculations of the fluoride content, the relevant reaction equations given by Scott (1979) were used. The equations are

$$3SiF_4(g) + 2H_2O(l) \rightleftharpoons SiO_2(s) + 2H_2SiF_6(aq)$$

$$H_2SiF_6(aq) + 6OH^-(aq) \rightleftharpoons 6F^-(aq) + SiO_2(s) + 4H_2O(l)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

The mmoles of fluoride ion present in the sample (first replicate) were determined, using the computer generated volumes from the second derivative method, and then the percentage fluoride determined to be 0.04% by mass for each of the first and second replicates. However, the third TCG replicate yielded a negative result of -2.5% fluoride.

- Kynoch phosphogypsum results

The average endpoint volume was 9.72 ± 0.03 with RSD of 0.3%. The amounts of fluoride in the three replicate samples of Kynoch phosphogypsum were obtained as described previously and determined to be -1.7%, -1.2% and 0.04% respectively.

9.2.3.5 Discussion

The potentiometric titrations of various replicates for the TCG and Kynoch samples resulted in good agreement between the titres with RSD of 0.5% and 0.3% respectively. Despite this excellent agreement, a positive low result of 0.04 % fluoride for the two replicates and a negative result for the last replicate for the TCG sample were obtained. The Kynoch phosphogypsum analysis yielded two negative results and a single positive result of 0.04% fluoride. A plausible reason for these low results and the negative values is that the fluoride content in these chemical gypsum samples was too low (which corroborates the ISE and IC methods) to be distinguished by this method. Hence, the titre data generated on the graph paper was insufficient to account for the very low fluoride amounts. A digital output, which was not available, might have been more suitable because manual estimation of the number of blocks on the chart paper for either the pH scale or the volume scale was prone to slight errors. A slight overestimation or underestimation could be detrimental. In order to be responsive to these low levels of fluoride, the experimental data should be interpolated to more than four digits. This problem led to the use of more digits in the volume data without the normal rounding off.

9.2.4 Fluoride Analysis – A spectrophotometric approach

The principle of the method is based on the decolourization of sulphonic acid azo chromotrop (SPADNS) by fluoride. The measurements were taken at 660 nm and 580 nm for comparison at each wavelength. The samples were prepared by the steam distillation of fluoride, as explained in the Willard and Winter method (Section 9.2.1). This approach therefore represents a Willard and Winter approach with spectrophotometric detection.

9.2.4.1 Instrumentation

The Genesys 10 Uv-ThermoSpectronic Uv-Vis spectrophotometer was used to determine the absorbances of the test solutions.

9.2.4.2 Samples and reagents

- Preparation of SPADNS

A 0.1336g mass of zirconium oxide chloride octahydrate was dissolved in approximately 500 mL of deionized water. A 350 mL of concentrated hydrochloric acid was added, followed by 0.9642g of SPADNS. The solution was shaken vigorously to dissolve all solids, and brought up to the mark in a 1L volumetric flask with deionized water .

- Samples

A spiking technique was used to prepare chemical gypsum samples. A 10.00 mL volume of the Kynoch sample, prepared as in Section 9.2.1, was pipetted into a 50.00 mL volumetric flask. A 5.00 mL volume of SPADNS was added to the Kynoch solution. A predetermined amount of fluoride ion standard solution was added to make the total fluoride ion concentration in the mixture 0.50 ppm. The solution was mixed and made up to the mark with deionized water. This represented sample No.1 in Table 9.2. Similarly, other samples of Kynoch phosphogypsum

(No.2 to No. 6) were prepared with exactly the same amount of the Kynoch sample but with differing amounts of added fluoride ion, as shown in Table 9.2.

Solution No.7 was a blank which did not contain any added fluoride ion. It was prepared by pipetting 5.00 mL SPADNS plus 10.00 mL of Kynoch phosphogypsum sample into a 50.00 mL volumetric flask and bringing it up to the mark with deionized water.

Solution No.8 was a blank which contained neither added fluoride nor chemical gypsum. It was prepared by pipetting 5.00 mL of SPADNS into a 50.00 mL volumetric flask, bringing it up to the mark with deionized water.

The TCG samples were prepared as for the Kynoch samples as shown in Table 9.2.

Table 9.2: Kynoch or TCG samples

Solution No.	Added fluoride (ppm)
1	0.5
2	1
3	2
4	3
5	4
6	5
7	SPADNS + 10 mL sample
8	SPADNS alone

9.2.4.3 Results

Each sample was left for about an hour to ensure that total decolourization of SPADNS had taken place. Then the absorbance of each Kynoch sample solution at 600 nm was measured and tabulated in Table 9.3.

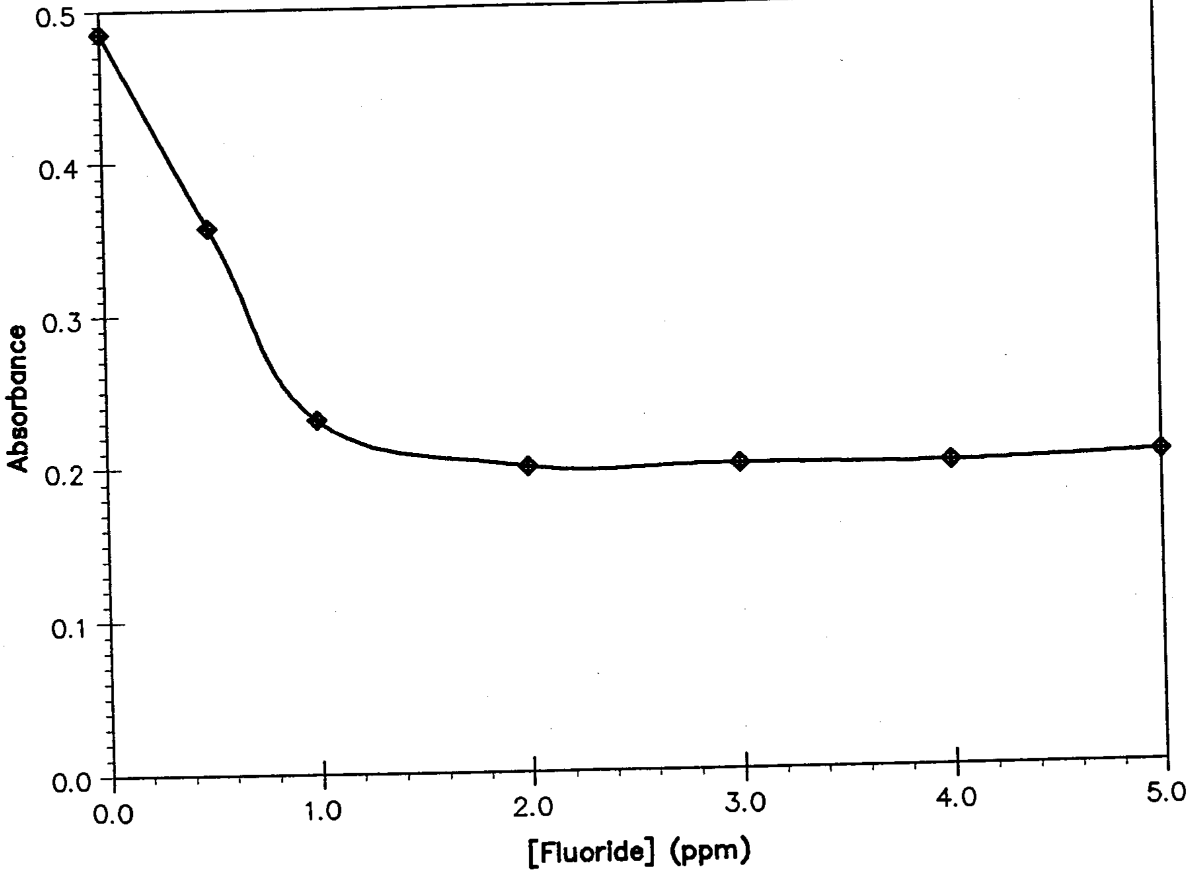
Table 9.3: Kynoch absorbances vs deionized water blank and SPADNS blank (660nm)

Solution No.	Abs vs water blank	Abs vs SPADNS blank
1	0.020; 0.020; 0.021	0.030; 0.028; 0.031
2	0.011; 0.012; 0.010	0.017; 0.016; 0.018
3	0.007; 0.006; 0.008	0.022; 0.021; 0.020
4	0.008; 0.007; 0.008	0.022; 0.022; 0.020
5	0.006; 0.007;0.007	0.022; 0.020; 0.021
6	0.006; 0.007;0.006	0.022;0.021; 0.021
7	0.027; 0.027; 0.026	0.001; 0.001; 0.001
8	0.028;0.028;0.028	-

The absorbance results obtained at 660 nm, reflected in Table 9.3, were observed to be too low in general. SPADNS was then scanned at various wavelengths to study the absorbance pattern. It was observed that SPADNS absorbed much better at 580 nm. Hence, both Kynoch and TCG samples were analyzed at 580nm. The results are given in Table 9.4. The change in absorbance for Kynoch samples, from the data in Table 9.4, was plotted as an example in Figure 9.1.

Figure 9.1

Decolourisation of SPADNS by fluoride (Kynoch at 580 nm)



At 580 nm, the change in absorbance due to fluoride ion present in the Kynoch phosphogypsum sample was

$$0.529 - 0.485 = 0.044$$

The change in absorbance attributable to added fluoride with a concentration of 1.00 ppm was

$$0.529 - 0.231 - 0.044 = 0.254$$

Table 9.4: Kynoch and TCG absorbances vs deionized water blank (580nm)

Solution No.	Abs vs water blank for Kynoch samples	Abs vs water blank for TCG samples
1	0.362	0.437
2	0.231	0.231
3	0.204	0.203
4	0.199	0.199
5	0.198	0.197
6	0.202	0.199
7	0.485	0.525
8	0.529	0.529

The concentration of fluoride in the Kynoch phosphogypsum was calculated as

$$\frac{0.044 \times 1.00\,mg/L \times 50.00\,mL}{0.254 \times 10.00\,mL} = 0.87\,ppm$$

The amount of fluoride was computed as a percentage and found to be

$$\frac{0.8661\,mg/L \times 0.250\,L \times 100\%}{0.2560\,g \times 1000\,mg/g} = 0.085\%$$

Similarly, the amount of fluoride was calculated for sample No.1 (0.50 ppm added fluoride) with a result of 0.89 ppm; the percentage of fluoride was 0.087%. The average fluoride content for Kynoch phosphogypsum was 0.086±0.001%F^- by mass.

Similarly, the percentage of fluoride in Tioxide chemical gypsum, TCG, was determined as 0.009±0.002%F^- (m/m) from data given in Table 9.4.

9.2.4.4 Discussion

The absorbance of the Kynoch samples relative to deionized water or sulphonic acid azo chromotrop (SPADNS) shown in Table 9.3, decreased with the increased amount of added fluoride ion and leveled off to a plateau. This trend was repeated in both Kynoch and TCG samples when measurements were taken at a more sensitive wavelength of 580 nm (Table 9.4). This change in absorbance has been shown in Figure 9.1 above, with the Kynoch sample used as an example. Clearly, the results indicate a decolourization reaction of the dye, SPADNS, by fluoride ion.

Ideally, the spectrophotometric method, utilizing SPADNS for fluoride analysis, is a reaction rate method which requires meticulous measurements of absorbance at a specific reaction time. The reaction time must be optimized and fixed for all samples in order to allow for reproducible extent of reaction between the fluoride and SPADNS. The rate approach hurdle was circumvented by allowing enough time for the reaction to reach completion. This adaptation allowed for analysis by means of a basic bench top spectrophotometer. The amount of fluoride in the Kynoch phosphogypsum was determined to be 0.086±0.001%F^-(m/m) while the Tioxide titangypsum contained 0.009±0.002%F^- by mass.

9.3 Conclusion

The Willard and Winter steam distillation method of sample preparation was long and tedious. The potentiometric analysis method produced inconsistent results for both the Kynoch phosphogypsum and the Tioxide titangypsum samples. The inconsistency of the results could be attributed to the inability of the method to measure the low levels of fluoride in the chemical gypsum samples under study. The spectrophotometric analysis was consistent for both Kynoch phosphogypsum and Tioxide titangypsum samples, giving fluoride levels of 0.086±0.001%F^- and 0.009±0.002%F^- by mass respectively. The results obtained by the spectrophotometric approach largely corroborated those obtained previously by the ISE method (0.008±0.000%F^- for Tioxide titangypsum and 0.104±0.000%F^- for Kynoch phosphogypsum). The spectrophotometric results are much lower compared to those obtained by the IC method (0.016±0.008%F^- for Tioxide titangypsum and 0.129±0.010%F^- for Kynoch phosphogypsum).

CHAPTER 10 Investigation of fluoride volatility at temperatures used for sintering the samples

10.1 Introduction

The possibility of losing fluoride due to the formation of a volatile compound at the high temperatures which are used for the sintering of the samples, has been mooted (Peters and Ladd, 1971). Such a loss may result in quantitatively inaccurate results. In this study, an investigation was carried out to determine whether any fluoride would be lost when sodium fluoride is subjected to a temperature of 900°C during fusion. Fluoride analysis was conducted by both ISE and IC methods. In the case of the ISE analysis, the effectiveness of two different total ionic strength buffers was compared.

10.2 ISE method – Experimental

10.2.1 Reagents and samples

- **NaF (No. 1)**

A 0.2246g mass of a previously dried NaF salt was weighed and transferred into a platinum crucible. To this was added 0.50 g ZnO, followed by 2.50g of sodium carbonate. The mixture was sintered at 900°C in a muffle furnace for 30 minutes. The melt was allowed to cool and then transferred to a 500mL beaker with deionized water. After adjusting the pH to 5.1 with nitric acid, the solution was filtered and then transferred to a 1L volumetric flask and made up to volume with deionized water. The expected concentration of NaF was 102 ppm.

- **NaF (No. 2)**

This was prepared in the same way as described above. The weighed mass of NaF was 0.2210g and the pH was adjusted to 5.1. The expected concentration of NaF was 100 ppm.

- **Kynoch phosphogypsum (FPSU) sample**

This was prepared in the same way as the NaF samples. A 0.6207g sample of Kynoch batch 3 phosphogupsum, FPSU, was weighed. The pH was adjusted to 5.1 with nitric acid and the solution made up to 250mL with deionized water.

- **Buffer 1 and Buffer 2**

Each total ionic strength buffer was prepared as described previously in Section 5.2.4

10.2.2 Instrumentation

Metrohm 692 pH/Ion Meter with a Metrohm Fluoride ISE 6.0502.150 indicator electrode coupled to a Metrohm reference electrode 6.0733.100 were used.

10.2.3 Analysis procedure

A series of fluoride standard solutions were prepared with a concentration range spanning 1.00 to 6.00 ppm fluoride (Table 10.1). A 20.00 mL portion of each standard solution was pipetted into a 50 mL plastic beaker, followed by an equal amount of Buffer 1. Fluoride ion selective indicator electrode and a reference electrode were immersed in the solution. The solution was stirred on a magnetic stirrer, and the potential measured. The analyses were carried out at ambient temperature as explained in Section 7.5. Similar solutions of fluoride ion standards were prepared and mixed with Buffer 2. The potential of each of the solutions was measured.

Each of the two NaF sample solutions prepared above was diluted 50 times with deionized water and poured into two separate 100mL volumetric flasks. A 20.00 mL portion of the diluted NaF sample (NaF No.1 and NaF No. 2) was pipetted into a 50 mL plastic beaker, followed by an equal amount of Buffer 1. The potential of each sample mixture was measured. The procedure was repeated for Buffer 2.

A 20.00 mL portion of the FPSU sample was mixed with an equal amount of TISAB (Buffer 1 in one case and Buffer 2 in the other) and the potential of the diluted sample determined as explained above. The measurements were taken in triplicate for each buffer solution.

10.2.4 Results

The raw data results are tabulated in Table 10.1 and Table 10.2. The calibration data for the standard solutions diluted with Buffer 1 were plotted as shown in Figure

10.1. The concentration of fluoride ion in the NaF samples was determined from the least square line equation as explained previously. The results for standard solutions diluted with Buffer 2 were treated in the same way.

Table 10.1: Raw data for various samples/standards.

[Fluoride] ppm	Potential (mV) - Buffer 1	Potential (mV) - Buffer 2
1.00 std	115.0; 114.8; 114.9 or 114.9±0.1 RSD = 0.1%	103.4; 103.2; 103.3 or 103.3±0.1 RSD = 0.1%
2.00 std	99.8; 99.9; 99.7 or 99.8±0.1 RSD = 0.1%	89.0; 88.9; 88.8 or 88.9±0.1 RSD = 0.1%
4.00 std	81.4; 81.4; 81.5 or 81.4±0.1 RSD = 0.1%	71.7; 71.6; 71.6 or 71.6±0.1 RSD = 0.1%
5.00 std	74.9; 74.8; 74.9 or 74.9±0.1 RSD = 0.1%	65.4; 65.5; 65.4 or 65.4±0.1 RSD = 0.1%
6.00 std	70.4; 70.2; 70.3 or 70.3±0.1 RSD = 0.1%	61.4; 61.4; 61.5 or 61.4±0.1 RSD = 0.1%
NaF No. 1 sample	97.8; 97.6; 97.7	87.1; 87.2; 87.0
NaF No. 2 sample	98.2; 98.1; 98.0	87.4; 87.5; 87.6
FPSU sample	98.2; 98.3; 98.3	87.5; 87.4; 87.6

The average results for the standards are summarized in Table 10.2.

Table 10.2: Average potential for various fluoride standard solutions

[Fluoride] ppm (Diluted)	log $[F^-]$	Average Potential (mV) - Buffer 1	Average Potential (mV) - Buffer 2
0.50	-0.301	114.9	103.3
1.00	0.000	99.8	88.9
2.00	0.301	81.4	71.6
2.50	0.378	74.9	65.4
3.00	0.477	70.3	61.4

The results for each sample are summarized in Table 10.3. The amount of fluoride (% m/m) in the FPSU sample was determined as explained previously and the results are given in Table 10.4.

Table 10.3: Concentration of fluoride ion from various samples for each buffer solution

Sample	$[F^-]$ ppm (Buffer 1)	$[F^-]$ ppm Buffer 2
NaF No.1	102.1 ± 0.4 with RSD of 0.4%.	101.8 ± 0.5 with RSD of 0.4%.
NaF No.2	100.5 ± 0.4 with RSD of 0.4%.	100.2 ± 0.4 with RSD of 0.4%.
FPSU	1.996 ± 0.005 with RSD of 0.2%.	2.004 ± 0.009 with RSD of 0.4%.

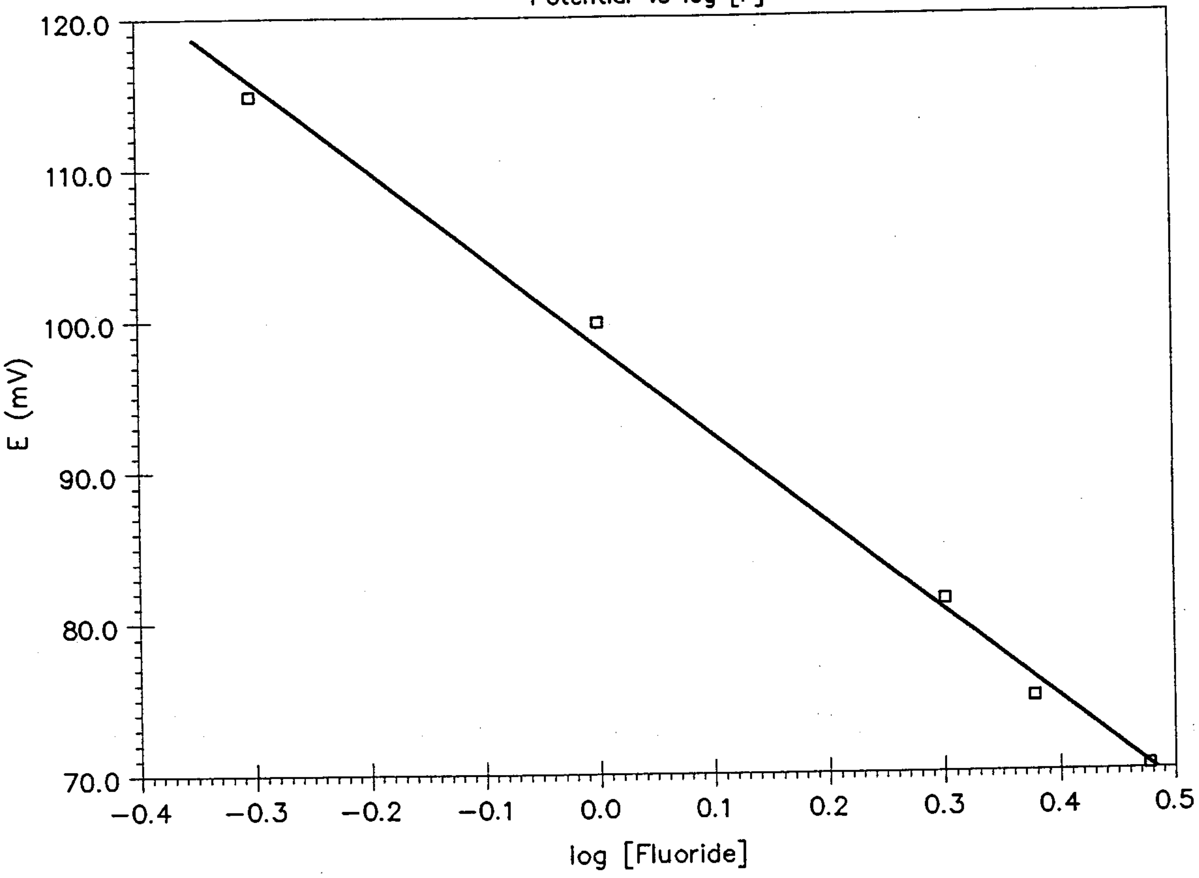


Figure 10.1: Fluoride volatility (Buffer 1)

Potential vs log [F]

Table 10.4: Percentage of fluoride in FPSU samples for Buffer 1 and Buffer 2

Sample	%F^- (Buffer 1)	%F^- Buffer 2
FPSU	0.080 ± 0.000	0.081 ± 0.000

10.2.5 Discussion and conclusion

The two samples, NaF No.1 and NaF No.2, were prepared such that each contained 102 and 100 ppm fluoride ion respectively. The experimental data results for both Buffer 1 and Buffer 2 yielded an average of 102 ppm for NaF No.1, which amounted to 100% recovery. For NaF No.2 sample, the concentration of fluoride ion was 100 ppm for Buffer 1 and Buffer 2 respectively, which amounted to 100% recovery in each case. Hence, results for both NaF samples produced 100% recovery with each of the buffer solutions. It can therefore be concluded that no loss of fluoride due to volatilization could be accounted for in the sample preparation method used. The fusion mixture used, ZnO and Na_2CO_3 at the working temperature of 900 °C, proved to be very effective and most efficient in avoiding any potential fluoride loss due to volatilization in the muffle furnace.

The results for the FPSU phosphogypsum sample gave very close values for the fluoride amount (0.080 ± 0.000%F^- Buffer 1 and 0.081 ± 0.000%F^- Buffer 2) regardless of the type of the buffer solution used. Hence, the two buffer solutions were equally effective in controlling the ionic strength and any possible interferents during the measurement of potentials by the ISE method.

10.3 Ion Chromatography – Experimental

10.3.1 Samples and reagents

10.3.1.1 Samples

Each of the two samples, NaF (No.1) and NaF (No.2) described in Section 10.2.1, was diluted 50 times with deionized water and chromatographed.

10.3.1.2 Standards

Fluoride standards with concentrations of 1.00, 2.00, 3.00 and 4.00 ppm were prepared and chromatographed.

10.3.2 Chromatographic conditions

The eluent was prepared as a mixture of carbonate and bicarbonate whose final composition was 3.5 mM CO_3^{2-} and 1.0 mM HCO_3^-. The flow rate was maintained at 1.2 mL/minute. The sample size was 50 microlitres throughout. The separator used was the AS14 column and AG14 guard. The membrane suppressor was regenerated with a 0.0250M H_2SO_4 solution.

10.3.3 Instrumentation

The instrumentation used was the Dionex 4000i HPIC with a conductivity detector.

10.3.4 Results

The raw data results obtained from the chromatograms of the fluoride standard solutions and the NaF samples are given in Table 10.5.

Table 10.5: Peak height data for normal calibration method.

Standard or Sample	Peak height (PH)	Average PH for standards
1.00 ppm fluoride std	230074.3; 233905.9	231990.1
2.00 ppm fluoride std	401504.1;401504.1	401504.1
3.00 ppm fluoride std	643292.9; 641147.7	642220.3
4.00 ppm fluoride std	806774.6; 806246.7	806512.2
NaF (No.1) sample	414316.2; 414994.7	
NaF (No.2) sample	396418.1; 401406.1	

The results were analyzed by the normal calibration method to determine the content of fluoride in each sample, as explained previously in Chapter 8. The equation used for the least squares line was derived from the data for the fluoride standards (Table 10.5) to be:

$$PH = 196428[F^-] + 29486$$

The standard deviation of the slope, s_m, was computed to be 10471. The standard deviation of the intercept, s_b, was 28677. The standard deviation about the measurement, s_r, was 23415. The correlation coefficient was determined as 0.997. From the calibration equation, the average concentration of fluoride in the 50 times diluted NaF (No.1) sample was determined to be 2.0 ppm, and that of NaF (No.2) sample as 1.9 ppm.

The standard deviation, s_c, of the result for NaF (No.1) sample was determined using equation 6.15 as follows:

$$s_c = \frac{s_r}{m}\sqrt{\frac{1}{M}+\frac{1}{N}+\frac{(\bar{y}_c-\bar{y})^2}{m^2 S_{xx}}}$$

where M = 2 (duplicate analyses), N = 4 (number of data points) and $\bar{y}$ is the mean of y for N calibration data. The value of $\bar{y}_c$ is obtained from the average of peak height as

$$\bar{y}_c = \frac{414316.2 + 414994.7}{2} = 414655.4\,.$$

Then s_c is

$$s_c = \frac{23415}{196428.25}\sqrt{\frac{1}{2}+\frac{1}{4}+\frac{(414655.4-520556.7)^2}{196428.25^2 \times 5.00}}$$
$$= 0.1$$

Hence, the amount of fluoride in the diluted (50 times) NaF (No.1) sample was 2.0±0.1 ppm F^-. Similarly, for NaF (No.2) sample the amount of fluoride in the diluted sample was 1.9±0.1 ppm F^-.

10.3.5 Discussion and conclusion

The percentage recovery of fluoride from the sintered (900°C) NaF No.1 sample was found to be 100% for both Buffer 1 and Buffer 2 (ISE method). The fluoride amount for NaF No.1 sample obtained by the IC method was 2.0±0.1 ppm F^- after dilution or 100.0±5.0 ppm F^- in the original solution as compared to an expected 102ppm fluoride based on the manner in which the sample was prepared. Similarly, for NaF No.2 sample, the percentage recovery was 100% for both Buffer 1 and Buffer 2 (ISE method). The IC results were 1.9±0.1 ppm F^- after dilution or 95.0±5.0 ppm F^- in the original solution as compared to 100ppm from the manner in which the sample was prepared. Hence, within experimental error, no fluoride loss is indicated. Hence, the sintering method used in the preparation of samples did not indicate loss of fluoride through volatilization.

Chapter 11 Conclusion

11.1 Removal of fluoride impurities from chemical gypsum

This study has shown that the methods used in the treatment of chemical gypsum to reduce the levels of associated fluoride impurities differ significantly in their respective effectiveness. Since the fluoride impurities may be attached to the surface of the chemical gypsum particles or may be solid soluted in the crystal lattice, various phases of gypsum play a role in the nature of the impurities finally taken down during the manufacture of the chemical gypsum.

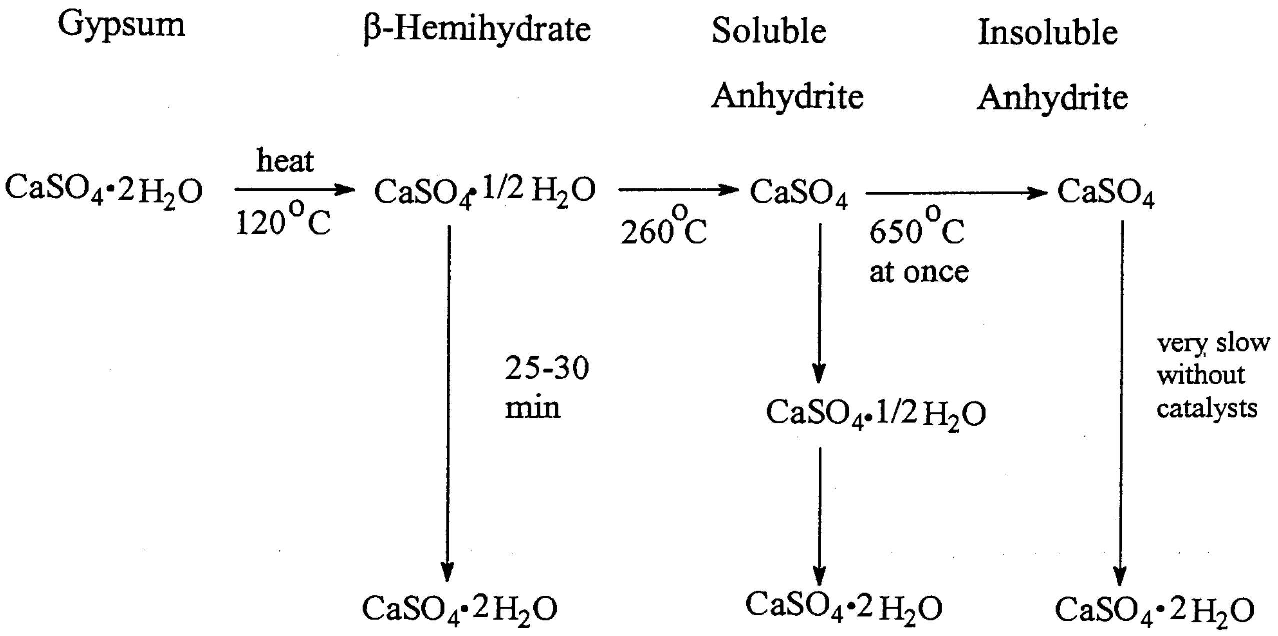
Gypsum ($CaSO_4 \cdot 2H_2O$) is the most common sulphate mineral and has traditionally been extracted from the ground. In recent times, gypsum has also been generated as chemical gypsum, a by-product of various industrial processes, as described in Chapter 1. Two other mineral forms of calcium sulphate commonly found are bassanite (calcium sulphate hemihydrate) and anhydrite (insoluble calcium sulphate anhydrite). Although the hemihydrate does occur naturally, it is generally prepared for commercial use by the dehydration of calcium sulphate dihydrate (Hand, 1997).

The removal of part of the total amount of crystalline water contained in gypsum results in a material that can be hydrated, i.e. the addition of free water to the powdered matter forms a paste or slurry which, upon setting, yields a solid mass of interlocking crystals of considerable strength (Nanni and Chang, 1985). The different hydration phases of calcium sulphate can be summarized as (Luckevich, 2000):

- the dehydration of the dihydrate ($CaSO_4 \cdot 2H_2O$) to either the hemihydrate ($CaSO_4 \cdot \frac{1}{2}2H_2O$) or the anhydrous form ($CaSO_4$)
- the hydration of the hemihydrate to gypsum and
- the hydration of anhydrite to either hemihydrate or gypsum.

These hydration phases are shown diagrammatically in Figure 11.1.

Figure 11.1: Hydration phases of gypsum (Luckevich, 2000)



All temperatures are approximates

Within a given hydration state there are observed differences in physical and chemical properties. These differences are a function of aspects such as chemical, crystallographic and physical variations.

The properties of the hemihydrate depend on conditions such as the temperature and relative humidity under which it is formed (Luckevich, 2000). There are two commonly known hemihydrates, namely the α-hemihydrate and the β-hemihydrate. The α-hemihydrate is well crystallized and formed under autoclave conditions at high temperature and steam pressure, or in acid, alkali or salt solutions at atmospheric pressure. The β-hemihydrate is formed under ambient pressure and relatively low humidity conditions. The hemihydrate is a metastable (not thermodynamically stable) form. The identification of the hemihydrate as an α-hemihydrate or a β-hemihydrate can be made reliably by the use of differential scanning calorimetry (DSC), as the two hemihydrates produce qualitatively different traces when heated. The process of rehydration of the hemihydrate to a dihydrate (gypsum) is relatively rapid and occurs through a recrystallization process. Upon dispersion in water, the hemihydrate dissolves to a liquid phase saturated in calcium and sulphate ions. Gypsum is less soluble than the hemihydrate, hence it immediately precipitates, removing calcium and sulphate ions from the solution. This causes the hemihydrate to dissolve and drives the hydration reaction to completion. The reaction is exothermic and the heat generated can be used to monitor the hydration process.

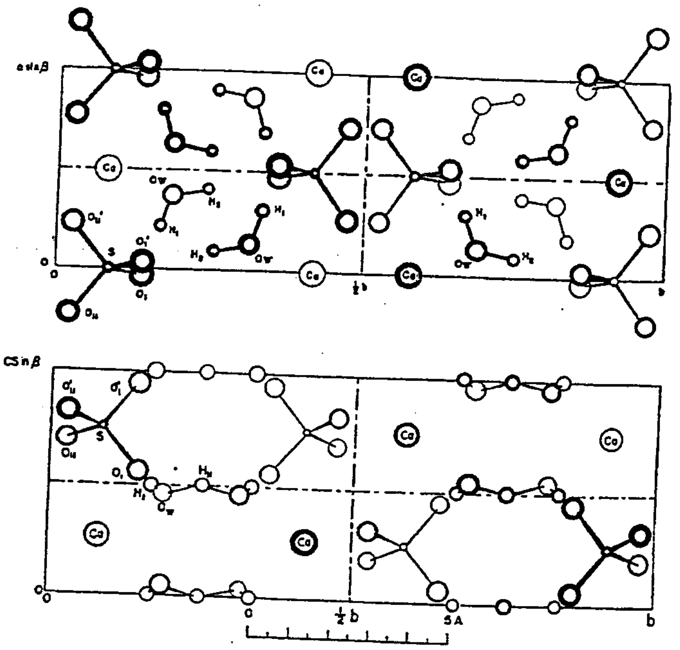
There are two distinct types of anhydrite, soluble and insoluble (Luckevich, 2000). Soluble anhydrite readily absorbs vapour or liquid water, reconverting to the hemihydrate form. Insoluble anhydrite cannot be transformed directly to the hemihydrate. It converts to the dihydrate form through a solution process of recrystallization.

The rate of conversion of the anhydrite to the dihydrate is relatively slow and depends on particle size, the temperature at which it was formed as well as the temperature, composition and pH of the hydration solution. A temperature of approximately 120 °C is required to calcine pure gypsum into hemihydrate (Nanni and Chang,1985). Higher temperatures will produce anhydrite, which becomes the stable composition for temperature values above 250 °C.

However, Hand (1997) states that there are three distinct anhydrite phases in existence. These are soluble γ-anhydrite, insoluble β-anhydrite and a high temperature α-anhydrite. In German and Japanese literature these are referred to as anhydrite III, anhydrite II, and anhydrite I respectively. Anhydrite II and anhydrite III are stable at room temperature, but the soluble anhydrite III readily rehydrates to produce hemihydrate. Gadalla et al.(1987) state that the crystal structures of the hemihydrate and γ-anhydrite have close lattice parameters which in fact may cause difficulty in identifying the hemihydrate which is considered by "some authors as a meta-stable phase".

The crystal structure of gypsum, $CaSO_4 \cdot 2H_2O$, shown in Figure 11.2, comprises pairs of adjacent layers which contain Ca^{2+} and SO_4^{2-} ions. The calcium ions are indicated as small circles and the sulphate groups as tetrahedral structures. The water molecules are located between successive pairs of layers in such a way that they are hydrogen bonded to the oxygen atoms of the sulphate groups. Each Ca^{2+} ion is coordinated by six oxygen atoms of SO_4^{2-} groups and by two water molecules.

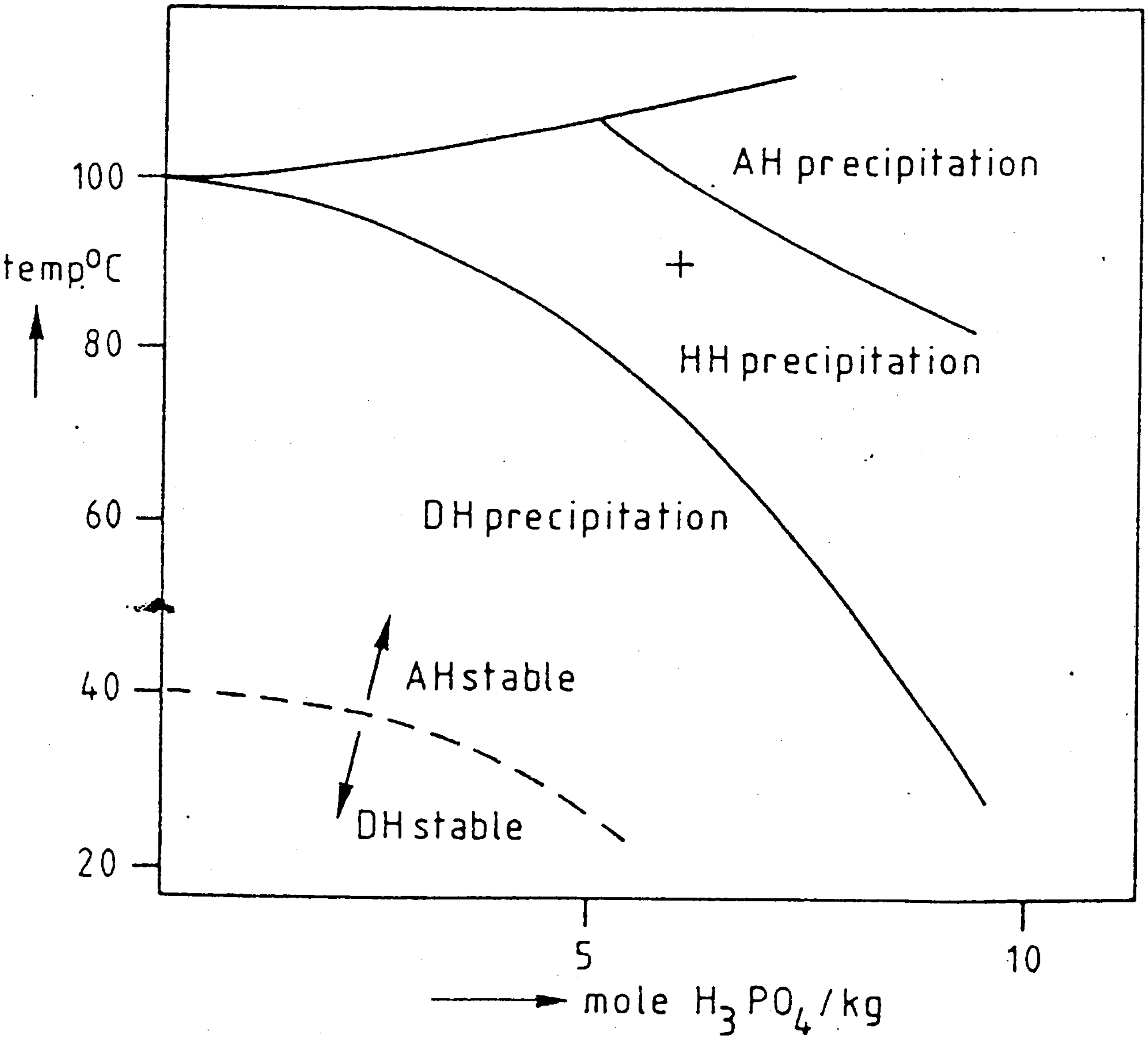
Figure 11.2: Crystal structure of gypsum from Atoji and Rundle (1958)



Van Der Sluis et al.(1986) studied crystallization of calcium sulphate in concentrated phosphoric acid. The process involved digestion of the phosphate ore (fluoroapatite) in recycled phosphoric acid which resulted in a clear calcium dihydrogen phosphate free of cadmium(II) ion impurities. Thereafter the calcium dihydrogen phosphate was reacted with sulphuric acid, under specific conditions, to produce a precipitate of calcium sulphate hemihydrate. The amount of foreign ions incorporated was found to depend largely on the operating conditions, given by the phosphoric acid and sulphuric acid content of the solution, the temperature, and the supersaturation. Impurities from the ore were also found to affect the uptake of foreign ions by calcium sulphate. Depending on the temperature and the H_3PO_4 and H_2SO_4 content of the solution, either calcium sulphate dihydrate, hemihydrate or anhydrite will be formed as shown in Figure

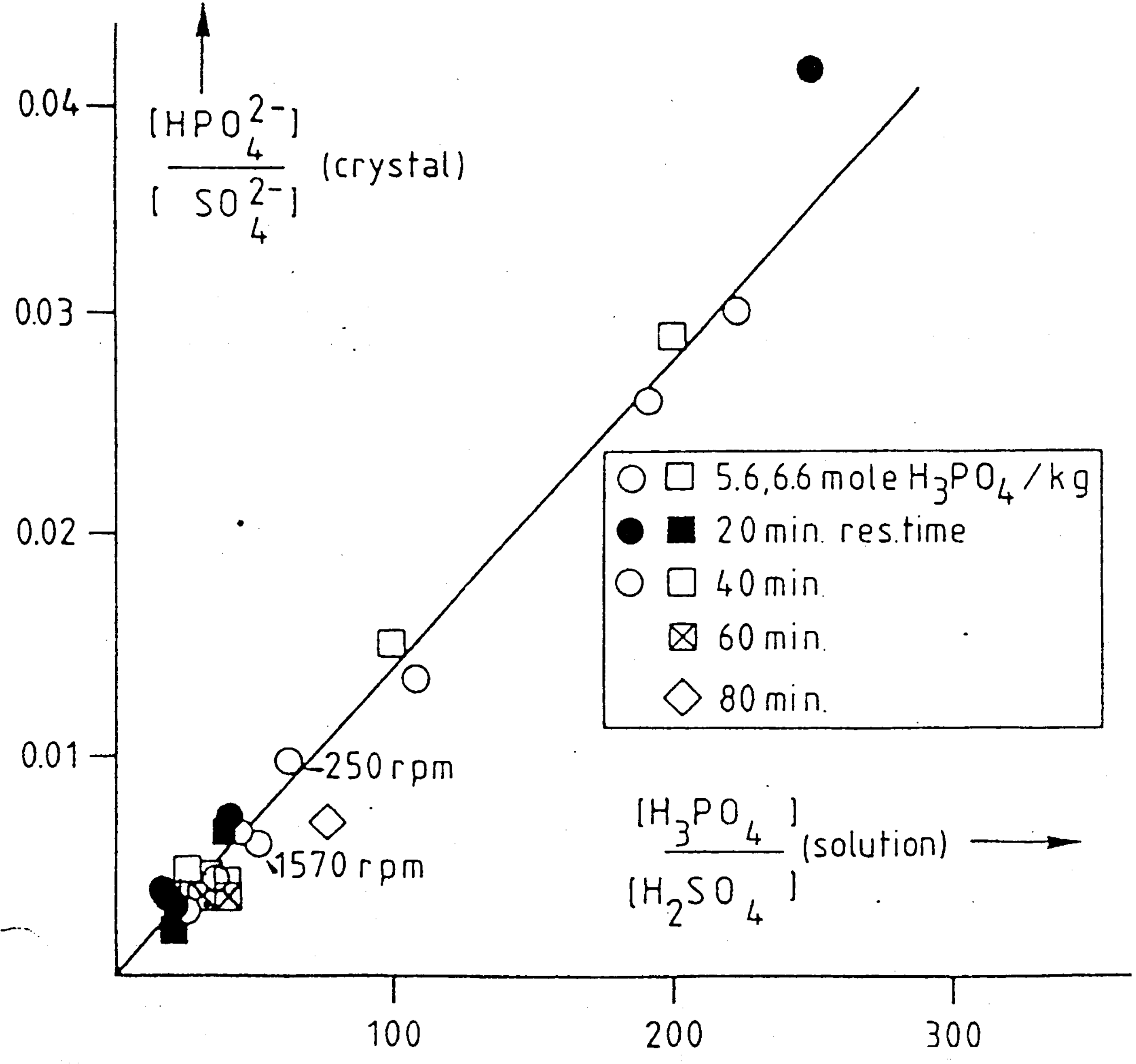
11.3. The solid lines in Figure 11.3 represent equilibrium curves, but since some of these modifications are metastable under the given conditions, the lines merely indicate which phase will initially precipitate. The dotted line indicates the regions where either the dihydrate or anhydrite phase is stable.

Figure 11.3: The precipitated calcium sulphate as a function of the H_3PO_4 content and temperature of the solution. Note that the hemihydrate phase exists only as a metastable phase, and that the anhydrite phase is stable over a wide range of conditions (Van Der Sluis etal., 1986)



HPO_4^{2-} ions can be incorporated in the $CaSO_4 \cdot 2H_2O$ crystal structure since the two ions, HPO_4^{2-} and SO_4^{2-}, are similar in size and share an affinity for calcium ions (Van Der Sluis et al., 1986). Their findings in this regard showing the molar [HPO_4^{2-}] over [SO_4^{2-}] ratio in the crystal structure versus the molar [H_3PO_4] over [H_2SO_4] ratio for various residence times are shown in Figure 11.4. The phosphate uptake decreases with increasing [H_2SO_4] and a linear dependence between the molar phosphate over sulphate ions in the crystals and in the solution appears to exist, as shown in Figure 11.4.

Figure 11.4: The phosphate incorporation, expressed as molar phosphate over sulphate ratio in the crystals, as a function of the same ratio in the solution for various residence times.



It has therefore been demonstrated in the discussion above that under certain conditions, HPO_4^{2-} can substitute for the SO_4^{2-} in the crystal structure shown in Figure 11.2. Singh and Garg (2000) mention that fluoride impurity in chemical gypsum in the form of AlF_5^{2-} may substitute for SO_4^{2-} in the gypsum crystal structure because of its similarity in size to the sulphate ion. The solid soluted impurities such as AlF_5^{2-} and HPO_4^{2-} are not removed during the washing with water of the chemical gypsum. In Section 7.9.3.5 it was shown that when Kynoch phosphogypsum (batch 1) is washed with water, 9% of soluble fluoride is removed. Kynock phosphogypsum thus seems to contain more than 90% fluoride that was taken up in the structure (water insoluble fluoride). On the other hand, the amount of water soluble fluoride removed from Omnia phosphogypsum was 21%. Omnia phosphogypsum seems to contain 79% water insoluble fluoride. The amount of fluoride in untreated Tioxide titangypsum samples has been shown to be very low with a maximum of 0.02% by mass.

To a large extent, the effectiveness of removing the water soluble fluoride will be influenced by the efficiency of the washing steps during the filtration and the washing of the filter cakes of the formed chemical gypsum. If the chemical gypsum is washed thoroughly with pure water (in multiple stages) at the chemical gypsum producing plant, the remaining amount of water soluble fluoride will be low. The efficiency of washing the chemical gypsum can be improved by using high quality water and mechanical agitation of the chemical gypsum-water mixture during the washing stages. Hence, the samples obtained for analysis of soluble fluoride have to be properly labeled in order to make valid comparative studies. Since chemical gypsum is produced by industry in huge quantities at any given time, it is very possible that the results of water soluble fluoride in different batches within the same plant may vary significantly.

Ölmez and Erdem (1989) mention that the water soluble impurities in phosphogypsum can be removed by washing with milk of lime. Erdogan (1994) studied the effect of impurities on the setting time of untreated phosphogypsum and recommended that the phosphogypsum which is to be used to control the setting time be washed with milk of lime. The lime treatment leads to the removal of some of the impurities, which in turn, results in an improvement in the initial and final setting times. In this study, lime wash had the effect of removing more fluoride from the Kynoch phosphogypsum (36%), as compared to 8% from Omnia phosphogypsum. It is proposed that the Omnia phosphogypsum has different intrinsic properties as compared to the Kynoch phosphogypsum that make the two phosphogypsums to behave differently to the water wash and the lime. It seems that the Omnia phosphogypsum tends to have a higher rate of dissolution in the water, which in turn exposes more of the water soluble impurities to be disposed of during the water wash as compared to the Kynoch phosphogypsum. However, during the milk of lime wash, it seems the water soluble impurities such as hexafluorosilicates break down to fluorides as,

$$SiF_6^{2-} + 6OH^- \rightarrow 6F^- + SiO_3^{2-} + 3H_2O$$

but more of the soluble fluoride tend to form insoluble compound as,

$$2F^- + Ca^{2+} \rightarrow CaF_2$$

in Omnia phosphogypsum than Kynoch phosphogypsum, thereby resulting in low removal of fluoride in Omnia compared to Kynoch phosphogypsum.

Omnia phosphogypsum has been shown in Section 7.10.6 to comprise 14.2% course particles ranging in size between 300µm<particle size≤600µm. These "lumps" contain ten times the amount of fluoride compared to finer particles with a particle size range

of p≤150μm. The amount of fluoride in Kynoch phosphogypsum was shown to be independent of particle size. Gadalla et al. studied beneficiation of phosphogypsum in order to reduce the impurities that adversely affect its use in building materials such as wallboard, cement (phosphogypsum used as set retarder) and prefabricated blocks (Gadalla et al., 1987). They observed that wet screening analysis of phosphogypsum indicated that the coarsest fraction of phosphogypsum (+300μ) contained pebbles, quartz and untreated rock, i.e. CaF_2, citrate insoluble P_2O_5 and uranium. Hence, the high amount of fluoride in the course particles of Omnia may be attributed to fluoride-containing untreated pebbles from the raw material (phosphate rock). The inefficiency of crushing the phosphate rock into fine particles before acidulation in the phosphoric acid manufacture may lead to unreacted particles of phosphate rock, which in turn may result in the formation of phosphogypsum with coarse material. The coarse material containing insoluble fluoride in the form of CaF_2 would not respond to water washing treatment effectively.

Jarosiński et al (1993) have shown the effective removal of impurities such as fluorides, rare earths and phosphates when the hemihydrate phosphogypsum is leached with sulphuric acid. Strydom and Potgieter (1999) studied the dehydration behavior of natural gypsum as well as Omnia phosphogypsum and, among other factors, reported that the Omnia phosphogypsum was constituted predominantly of the hemihydrate form (66%), compared to the dihydrate (16%) and anhydrite (15%) forms.

The Japanese patent number1966-54968 discusses a method for the elimination of impurities, such as phosphate and fluorine compounds, adsorbed or present in solid solution in phosphogypsum. In this patent, chemical gypsum is calcined at a temperature between 120 – 250 °C, converting it predominantly to the hemihydrate form with some of it existing as soluble anhydrous gypsum. When this is rehydrated with sulphuric acid, the calcium phosphate or fluorine compounds present in the solid solution prior to recrystallization of the gypsum dissolve in the sulphuric acid and do not return to the solid solution state. These impurities are thus evidently eliminated.

In this study, the sulphuric acid treatment of the chemical gypsum has been highly effective in the removal of fluoride impurities. The amount of fluoride leached during the sulphuric acid treatment of Kynoch phosphogypsum was 91%. In the case of Omnia phosphogypsum, the amount of fluoride removed by the sulphuric acid treatment was 72% of the original amount in the untreated phosphogypsum. Judging collectively from the research work carried out by Jarosiński et al. (1993) and the Japanese patent number 1966-54968, in which fluoride and phosphate impurities were removed from the hemihydrate phosphogypsum by the sulphuric acid treatment, as well as from the work of Strydom and Potgieter (1999), who found that a great proportion of the Omnia phosphogypsum they studied was predominantly in the hemihydrate form, it is similarly proposed that the proportion of the soluble hemihydrate phase of the chemical gypsum utilized in this study, was dissolved under the sulphuric acidic treatment conditions to produce a liquid phase saturated in calcium ions and sulphate ions. Since gypsum is less soluble than the hemihydrate, it immediately precipitates, removing calcium and sulphate ions from solution. Hence, the impurities are freed leaving a purer, recrystallized chemical gypsum.

This study has shown in Table 3.1 that the South African chemical gypsums investigated, Omnia, Kynoch and Tioxide titangypsum, are predominately composed of CaO and SO_3. These chemical gypsum differ in the quanties of impurity species. The chemical gypsums have also shown to behave differently to various pretreatment methods mentioned above. However, these chemical gypsum are currently being used, albeit in limited quantities, by the local cement manufacturers as set retarder. This suggests that the chemical gypsums do behave like natural gypsum and therefore the major structural information provided in Figure 11.2 may be used as the basis when examining the manner in which impurities are carried down during pretreatment of the chemical gypsums.

The impurities in chemical gypsum negatively affect the properties of the products formed when it is used in place of natural gypsum. When natural gypsum that is to be used for the production of hydraulic cement in gypsum board manufacture contains impurities, it has been observed that these impurities affect calcination properties and the quality of the produced hemihydrate (Luckevich, 2000). Soluble impurities tend to lower the calcination temperature of natural gypsum in a batch kettle calcination apparatus. Insoluble impurities, on the other hand, have no significant effect on the calcination operation of gypsum. Solutions formed by co-crystalline impurities in chemical gypsum adversely affect the calcination properties. For example, pentafluoraluminate (AlF_5^{2-}) in fluorogypsum, which may substitute for sulphate in the growing crystal, increases the calcination temperature with increasing amounts of the incorporated pentafluoraluminate (Luckevich, 2000).

The amount of fluoride impurities in chemical gypsum depends on factors such as the production process and the raw material. The main raw material used during the production of phosphate fertilizer is the phosphate rock. The phosphate rock used at the

Kynoch fertilizer plant is sourced from the Phalaborwa complex. In this study, the analysis of the phosphate rock for fluoride by ISE and IC methods indicated that the percentage of fluoride was 0.27% (0.266±0.005%F^- by ISE technique and 0.258±0.019%F^- by IC method, Table 8.17). The average chemical analyses of representative phosphate rock samples across the Phalaborwa complex have been reported as 0.24% for apatite rich massive pyroxenite and 0.38% for apatite rich phlogopite (Fourie and De Jager, 1896). The phosphate rocks exist as mixtures characterized by the predominance of a certain rock type.

11.2 Fluoride analysis methods

The Ion Selective Electrode (ISE) and the Ion Chromatography (IC) methods require that fluoride be present in solution as F^- in order to be detected by these techniques. If the fluoride contained in the chemical gypsum is in a complexed form it will not be detected by either of these techniques. At the preparation stage of the chemical gypsum samples, a finely ground chemical gypsum sample is mixed with zinc oxide and sodium bicarbonate and then sintered in an oven at 900°C. The specific surface area of chemical gypsum increases with increasing temperature (Singh and Garg, 2000). At these high sintering temperatures, fluoride impurities are transferred from the chemical gypsum into the melt of sodium bicarbonate-zinc oxide. The high surface area of chemical gypsum at high temperatures means that more fluoride impurities which may have been trapped inside the solid would become exposed to the sintering melt. When the cooled melt is dissolved in water, fluoride is carried down as sodium fluoride while the silicates and aluminates complex with zinc out of the solution. The fluoride thus produced is amenable to analysis and detection by the Ion Selective Electrode method using fluoride sensitive electrodes, and also by Ion Chromatography using a conductivity detector as demonstrated in Chapter 7 and Chapter 8 respectively. The sample preparation technique, therefore, allows for the quantification of most of the fluoride impurities contained in the chemical gypsum.

Each of the chemical gypsum samples used in this study consists of a complex matrix as indicated in the composition of the major species given in Table 3.1. Concentrated nitric acid was used to assist dissolution of the samples after the fusion step because the high concentration of CaO (36.48% in Tioxide titangypsum, 38.24% Kynoch phosphogypsum, 38.38% Omnia phosphogypsum) may make them to be resistant to fusion alone.

The standard Willard and Winter method (W-W) with spectrophotometric detection is based on the decolourization of sulphuric acid azo chromotrop by fluoride.The Willard and Winter method is the standard method of determination of fluoride in inorganic materials (Scott, 1979; Peters and Ladd, 1971). In this study, the Willard and Winter method was used to compare results to those obtained by the ISE and IC methods. The results have been summarized in Table 11.1.

Table 11.1: Comparison of results for ISE, IC and W-W methods

	%F (ISE method)	%F (W-W method)	%F (IC method)
Kynoch	0.10±0.00	0.09±0.00	0.13±0.00
Tioxide	0.01±0.00	0.01±0.00	0.02±0.01

In general, the amount of fluoride in Tioxide chemical gypsum is approximately tenfold less than in Kynoch chemical gypsum.The results obtained by the Ion Chromatography method generally exhibited highest uncertainty as compared to those obtained by the Ion Selective Electrode method and the standard Willard and Winter method with spectrophotometric detection.

The ISE method is rapid and relatively simple compared to both the IC and the Willard and Winter methods. The IC method is superior for indicating the general complexity of the sample, because in a single run the analyst can immediately see many of the ionic constituents present in the sample. Thus an anion or cation profile that provides information about the composition of the sample can be obtained in a very short time, avoiding the necessity of time consuming tests. Hence, the IC method affords the analyst the capability of simultaneous multi-ion analysis. However, the IC method proved more time consuming than the ISE method. The Willard and Winter method was much longer compared to both ISE and IC methods and tedious. It involved many experimental stages and thus held a higher risk of determinate errors. The good correlation coefficients of 1.00 for ISE normal calibration curves (sections 7.6.4; 7.7.4; 7.8.2.6; 7.8.3.6 etc.) and IC standard addition curves (sections 8.8.2; 8.9.1; 8.9.2; 8.9.3 etc.) indicated a good linearity of calibration curves. The performance of the IC system, as judged from the reproducibility of fluoride retention times of the chromatographic peaks proved to be very good as indicated in Section 8.5.3. The retention time of the fluoride chromatographic peaks reproduced excellently with RSD of 0.7% over sixteen consecutive injections under fixed chromatographic conditions.

The analytical measurement error associated with the ISE measurements in this study was estimated from equation 2.5 as explained in Section 2.2.1.3. For example, in Table

7.4 for Kynoch normal calibration results, the voltage measurements differed by 0.0 mV for sample 1, giving an analytical error of 0%. Sample 2 and 3 gave analytical error estimates of 1% and 0.4% respectively. Similarly, the results from tables 7.13, 7.22and 7.29 showed that the analytical error was in general not more than 1%.

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